

The Effects of Wetland Restoration on the Production and Bioaccumulation of Methylmercury in the Sacramento-San Joaquin Delta, California

By

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Abstract

Methylmercury (MeHg) production, export, and bioaccumulation were investigated at representative sites throughout the Sacramento-San Joaquin Delta in California, in relation to wetlands restoration efforts in the region. Sediment MeHg and MeHg:total mercury (THg) ratios were examined at paired sites inside and outside various flooded wetland tracts. Relative mercury (Hg) methylation potential was estimated in Hg-amended sediment slurry experiments. Concentrations of aqueous MeHg were assessed at a range of representative wetland tracts in inflowing vs outflowing water during tidal cycles. Relative biological Hg exposure levels throughout the region and spatially among habitats were assessed with naturally occurring small fish and invertebrate indicator species, which were tested for THg, MeHg, individual variability in Hg bioaccumulation, and nitrogen and carbon stable isotopic ratios.

Sediment MeHg concentrations and MeHg:THg ratios were found to be significantly greater in flooded tracts characterized by dense submergent or emergent aquatic vegetation, as compared to adjacent Delta channel, mudflat, or sandflat environments. Wetland sediments from vegetated flooded tracts exhibited 2-30 times greater potential to produce MeHg than aquatic sediments of adjacent channels and flats. At these same locations, concentrations of aqueous MeHg and aqueous MeHg normalized to suspended solids were found to be substantially elevated in outflowing tidal water (off the tracts), relative to inflowing water. Consistent with the literature for other estuarine systems, all of these measures indicated that highly vegetated, flooded wetland sediments functioned as net producers and exporters of MeHg to the wider Delta.

However, biological findings indicated no discernible localized increase in biotic MeHg concentrations in flooded wetland tracts vs adjacent aquatic habitats. Vigorous tidal action may effectively mix MeHg from net methylating habitats into local areas, creating larger spatial patterns. Most surprising was the finding of notably lowest overall Hg bioaccumulation throughout a broad region of the south and central Delta that contained numerous wetland restoration sites identified as net methylating environments. This indicates that the linkages between sediment MeHg, aqueous MeHg, and ultimate bioaccumulation by aquatic organisms may be quite complex. The regions with most highly elevated biotic Hg identified in this work can all be characterized as being dominated by ongoing new inflows of Hg from upstream San Francisco Bay-Delta tributaries. Inputs of both elemental Hg from historic gold mining in the Sierra Nevada and abandoned mercury mine cinnabar in the Coast Ranges appear to be of importance. This suggests that upstream remediation efforts on either side of the watershed may be more regionally meaningful than previously anticipated. A secondary zone of relatively elevated Hg bioaccumulation occurred in the estuarine entrapment / salinity transition zone.

Introduction

Mercury (Hg) contamination and, particularly, the bioaccumulation of toxic methylmercury (MeHg) in food webs is one of the primary water quality issues in the San Francisco Bay-Delta watershed of California. This is the result, in large part, of the Gold Rush era legacy of extensive Hg use in Sierra Nevada gold mining, as well as the now-abandoned Hg mines in the California coast ranges that supplied this Hg. It is clear that both regions remain major sources of ongoing Hg contamination, both locally and downstream (Slotton *et al.* 1995, 1997, 1998, 1999, Suchanek *et al.* 1997, Foe and Croyle 1998, Domagalski 1998, Roth *et al.* 2000). During the past 150 years, significant amounts of Hg, coming from mining operations on both sides of the state, have been deposited in Bay-Delta sediments. The extensive Sacramento-San Joaquin Delta levee system that originated in the 1860's effectively isolated and converted ("reclaimed") wetlands for the production of agricultural crops and other uses and, in so doing, dramatically altered the natural functioning of these wetlands. Many levees were likely constructed at locations which already contained significant Hg deposits, and some of these historic Hg-laden diked wetlands have long been isolated from normal tidal inundation.

In recent decades, substantial tracts of this levee-protected land have once again become flooded wetlands. This has occurred through the natural breaching of some of the Delta levees during storm/flooding events, as well as through the deliberate breaching of levees for the purpose of restoring wetland habitat. Plans are underway to similarly convert numerous additional tracts of leveed land to wetlands. Some previous, current, and planned future breaching projects include extensive manipulative restoration work, such as the current project at Prospect Island (US ACE & DWR 2001). Other breach sites are being allowed to return to vegetated wetland habitat along a more natural trajectory. The concern is that significant new wetland creation in the Delta may increase MeHg production and that this may result in increased MeHg bioaccumulation in aquatic organisms of the region, as well as their consumers, both wildlife and human.

Wetlands have been shown to be important sites of MeHg production (e.g. Zilloux *et al.* 1993; Hurley *et al.* 1995, Rudd *et al.* 1995, Cleckner *et al.* 1998). This has been linked to elevated rates of Hg methylation, primarily by sulfate-reducing groups of bacteria which typically occur near the oxic/anoxic interface in aquatic systems (Compeau and Bartha 1985; Gilmour *et al.* 1992). Highly organic and potentially sulfate-enriched wetlands can provide habitat for these microbes. MeHg production in wetlands has also been implicated as a major source of MeHg to adjacent and downstream environments (e.g. St. Louis *et al.* 1994, Krabbenhoft *et al.* 1999). In addition, the well known phenomenon of newly flooded and re-flooded terrestrial soils producing a surge in Hg methylation may be important in new restoration projects (Bodaly *et al.* 1984, 1997, Slotton 1991) as well as in existing flooded tracts which experience seasonal or inter-annual shifts in standing water level (Snodgrass *et al.* 2000).

A survey level, foundational study (the subject of this report) was conducted by UC Davis between 1998 and 2001 to begin to examine the potential effects of various flooded Delta tracts on the production and bioaccumulation of MeHg. Flooded tracts of varying age, ecological successional stage, and vegetation density were examined throughout the Delta region, together with adjacent aquatic habitats such as channels and sloughs. Sites were

distributed from tributary inflows to the estuarine entrapment zone where fresh and salt water mix. Sediment total Hg (THg), MeHg, MeHg:THg ratios, and relationships with organic carbon were examined at paired sites inside and outside various representative flooded wetland tracts. Relative Hg methylation potential was estimated in Hg-amended sediment slurry experiments. Concentrations of aqueous MeHg were assessed at a range of representative flooded wetland tracts in inflowing vs outflowing water during tidal cycles. Relative biological Hg exposure levels throughout the region and spatially among habitats were assessed with naturally occurring small fish and invertebrate indicator species, which were tested for THg, MeHg, individual variability in Hg bioaccumulation, and nitrogen and carbon stable isotopic ratios. The study was designed to provide an initial indication of prevailing Hg trends in the Delta, including relative MeHg bioaccumulation, and the potential role of wetland restoration sites on the Hg dynamics of the overall system.

This CALFED-funded project was initiated prior to and independent of the larger, multi-investigator, directed-action, CALFED Bay-Delta watershed Hg research conducted in 2000-2001. However, the UC Davis Delta Hg study provides a variety of foundational information that is complimentary to that effort. The studies have been collaborative for the past two years and our report is being submitted here in conjunction with the findings of the wider group.

Methods

Study Area and Selection of Sampling Sites

This initial study included sites which were distributed throughout the entire Sacramento-San Joaquin Delta (Figure 1). Sampling was conducted from tributary inflow regions in the north, east, and south, through the Central Delta region where many late successional stage wetland tracts occur, to the estuarine freshwater/saline mixing zone of the West Delta. In addition to general spatial coverage of the area, sites were chosen within numerous wetland tracts of varying ages and degrees of successional development, together with adjacent non-wetland control sites. Sampling locations are additionally displayed throughout the report in the various map figures.

Field and Laboratory Techniques

Surficial sediment samples were collected from the top centimeter of undisturbed Ekman grab samples, with additional samples taken directly by hand with Teflon core tubes. Sediment samples from grabs were placed immediately into clean glass containers with minimal headspace; sediment samples for methylation potential experimental work were maintained on ice in the field and in transit to the laboratory. Sediment samples for analysis of in situ MeHg concentration were frozen immediately in the field using dry ice.

Water was collected directly into trace metal clean glass bottles and field preserved with 0.5% HCl, utilizing clean sampling technique. Aqueous Hg samples were double bagged at minimum, chilled immediately, and shipped to Battelle Marine Laboratories for analysis of raw

MeHg. Total suspended solids (TSS) samples were taken in parallel with Hg samples and analyzed within 96 hours by UC Davis using standard filter-based technique.

Small and juvenile fishes were sampled with a variety of beach seines. Bivalves were collected primarily by hand during low tides. Crayfish were collected using baited traps. Additional invertebrates were sampled with a variety of hand nets. Biotic samples were maintained on ice in the field and during transit to the laboratory. For all invertebrate and small fish sampling, efforts were made to obtain consistent samples both seasonally and spatially among the sites. In addition to the primary indicator organisms, samples of several different species of small fishes were generally taken, from among those types which were most prevalent and important components of local food webs. In this initial characterization of biotic Hg throughout the Delta region, multi-individual composites were primarily used for the small fish and clam analyses. Clam composite samples typically utilized 10-25 purged individuals within the optimal size range. Small fish composites contained a minimum of six and typically 20-40 individuals in the key size ranges. Crayfish were analyzed individually. Individual variability in Hg was tested with numerous individual analyses at several diverse, representative sites.

Fish were cleaned, identified, and sorted within 24 hours of collection and were then maintained frozen with water in Ziploc bags to avoid freezer desiccation. Individuals were weighed and measured prior to processing. Clams were maintained live in clean water which was changed twice daily for four days to purge them of all major gut contents and associated sediment, and were then frozen for storage. Crayfish were also stored frozen. Crayfish tail muscle and clam soft tissues were excised with a clean scalpel prior to analysis. Crayfish digestive tracts were removed. Small fish were prepared whole body, as were the clams (minus shells). Crayfish Hg was analyzed in tail muscle. Small fish and invertebrate samples were dried at 60 °C, powdered, and analyzed consistently on a dry weight basis. Sediment samples were analyzed in well homogenized fresh/wet samples. Moisture percentage was determined for all sample types to allow conversion of wet or dry weight analytical results. It is important to note that, in the current draft of this report, biotic THg and MeHg data are presented in DRY WEIGHT concentrations. The samples were analyzed as consistent dry powders, primarily for maximum homogeneity and to allow the accurate splitting of samples for different analyses. While we plan to eventually revise the numerous figures to reflect fresh/wet weight concentrations, be advised that the displayed data must be divided by approximately 5 to obtain corresponding wet weight values for the small fish and crayfish samples, and by approximately 10 for the clams. The primary objective has been to investigate *relative* concentrations, spatially and temporally, for which the dry weight data have been ideal.

Sediment and biotic THg samples were digested in 2:1 sulfuric:nitric acid under pressure (capped vessels) at approximately 90 °C for one hour, and then for an additional hour, uncapped, with the addition of potassium permanganate and potassium persulfate. Mercury was analyzed using a FIMS cold vapor atomic absorption (CVAA) system. Sediment and biota moisture percentage were determined with oven drying and sequential weighings. Sediment loss on ignition (LOI) was determined with sequential weighings and 475 °C muffle furnace ashing. Laboratory experiments using sediment slurries to estimate maximal potential MeHg production rates were conducted with 2:1 mixtures of site water:site sediment (top 1 cm). Mixtures were spiked with mercury chloride to 1.00 µg Hg g⁻¹. After placing identical aliquots into multiple

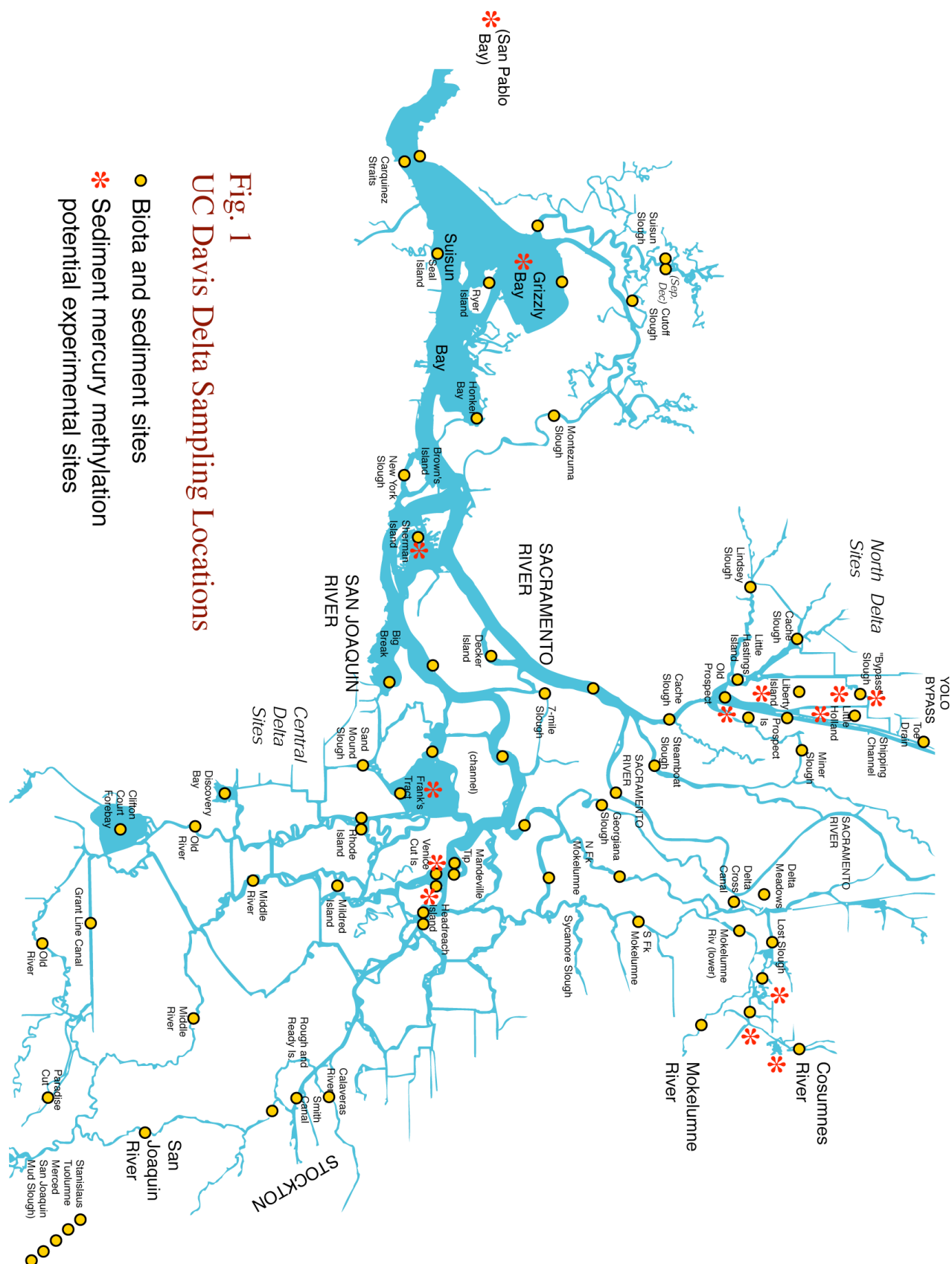
incubation chambers and sparging to uniform anoxia with nitrogen, samples were incubated at 22 °C for varying lengths of time. Individual methylation experiments were stopped by freezing at defined endpoints. Total Hg and N and C stable isotopes were analyzed at UC Davis. Methylmercury concentrations in sediment, water, and biological samples were analyzed by Battelle Marine Science Laboratories in Sequim Washington.

Quality Assurance / Quality Control

A rigorous program of QA/QC was utilized throughout the project. Standard field, preparatory, and analytical QA/QC included the collection of numerous field replicate samples and field blanks, careful preservation and assessment of actual moisture percentages of sediment and biotic samples, and extensive analytical split samples, spikes, spike replicates, calibration samples, blanks, laboratory control samples, and a range of standard reference materials with certified Hg contents. UC Davis laboratory QA/QC results for solid sample THg analyses are summarized in Table 1. The THg analytical results were consistently well within all control levels. Biotic, sediment, and aqueous MeHg QA/QC results from Battelle Marine Sciences Laboratories are available in individual analytical run files, located in the Appendix. Methyl Hg analytical QA was more variable than that for THg, consistent with the inherent greater variability of the MeHg methodology. However, Battelle QA was generally well within control levels and, when QA was found to be out of control, corrective actions were taken and samples were re-analyzed.

Table 1. Laboratory QA/QC summary for UC Davis Delta Project total mercury analyses.

	<u>Std Curve</u> <u>R²</u>	<u>Lab Split</u> <u>RPD</u>	<u>Field Dup.</u> <u>RPD</u>	<u>Spike</u> <u>Recoveries</u>	<u>Lab Cont. Std.</u> <u>Recoveries</u>
Certified Level (ppm)					
Ideal Recovery	1.000	(00%)	(0%)	(100%)	(100%)
Control Range	(> 0.975)	< 25%	< 25%	75-125%	75-125%
Tracking Method		Control Chart		Control Chart	Control Chart
Control Range (ppm)					
Recoveries (%)	0.9970-0.9999	0.0%-15.0%	0.2%-95.4%	88%-105%	95%-112%
Recoveries (ppm)			(higher near MDL)		
(n)	n=40	n=224	n=98	n=220	n=115
Mean Recoveries (%)	0.9995	2.90%	13.58%	96.4%	101.3%
Mean Recoveries (ppm)					
<i>Standard Reference Materials</i>					
		<u>BCR</u> <u>Cod</u>	<u>TORT-2</u> <u>Lobster</u>	<u>DOLT-2</u> <u>Dogfish</u>	<u>NIST 2976</u> <u>Mussel</u>
Certified Level (ppm)		0.56±0.02	0.27±0.02	2.14±0.28	0.061±0.004
Ideal Recovery		(100%)	(100%)	(100%)	(100%)
Control Range (%)		75-125%	75-125%	75-125%	75-125%
Tracking Method		Control Chart	Control Chart	Control Chart	Control Chart
Control Range (ppm)		0.42-0.70	0.20-0.34	1.61-2.68	0.05-0.08
Recoveries (%)		89%-94%	88%-111%	93%-108%	85%-126%
Recoveries (ppm)		0.50-0.53	0.24-0.30	2.00-2.31	0.05-0.08
		n=12	n=112	n=106	n=60
Mean Recoveries (%)		91.7%	101.7%	97.9%	96.7%
Mean Recoveries (ppm)		0.51	0.27	2.10	0.06



Results and Discussion

Sediment Total Mercury, Methylmercury, and MeHg:THg Ratios

Dry weight, whole-sediment Delta THg concentrations all occurred within a range of 0.01 to 0.33 $\mu\text{g g}^{-1}$ (ppm, Figure 2). It is important to note that particle size varied in these samples, from fine clay/silt in depositional areas to coarse sand in some of the more erosional locations. Metals, including Hg, tend to be most concentrated in fine grained particles (Theis et al. 1988, Roth et al. 2000). Future sampling will normalize to grain size and a variety of other sediment parameters. The whole-sediment Hg values, however, are useful as direct measures of the environment the organisms are exposed to. Greatest concentrations occurred at North Delta and East Delta inflow regions and in depositional regions where finest particle sizes dominated. This particularly included West Delta sites (0.18-0.33 $\mu\text{g g}^{-1}$), with moderate levels interspersed within the Central Delta (0.08-0.26 $\mu\text{g g}^{-1}$). South Delta sites were uniformly low in THg (0.02-0.15 $\mu\text{g g}^{-1}$).

Sediment MeHg concentrations were compared between various flooded tracts and adjacent non-wetland aquatic habitats throughout the Delta during a consistent late summer period (Figure 3). On a dry weight basis, sediment MeHg concentrations ranged between less than 0.1 and 7.7 ng g^{-1} (ppb). Lowest concentrations were seen in non-wetland channel and mudflat habitats, particularly in the West-Central and West Delta. Flooded tracts that did not demonstrate elevated sediment MeHg, relative to adjacent channel habitats, included the large mudflat-dominated tracts of the North Delta and Mildred Island in the Central Delta. However, in flooded Delta tracts that were characterized by dense submergent and/or emergent aquatic vegetation and highly organic sediments, sediment MeHg was dramatically greater than at adjacent non-wetland control sites. These sites included all of the most elevated sediment MeHg sampled, with vegetated wetland tracts exhibiting to over ten times greater MeHg concentrations than adjacent control sediments. Absolute sediment MeHg concentration has been used as an indicator of relative sediment methylation rates in aquatic sediments (e.g. Gilmour et al. 1998).

In Figure 4, sediment MeHg:THg ratios are displayed for the same paired sets of inside/outside flooded wetland tracts. The MeHg:THg ratio of surficial bottom sediments has also been utilized as a gross index of methylation activity in freshwater and estuarine sediments (e.g. Krabbenhoft et al. 1999, Canavan et al. 2000). Methyl percentages ranged from less than 0.1% to over 3.5%. The spatial pattern of sediment MeHg:THg closely followed that described above for sediment MeHg. The most elevated ratios occurred within flooded tracts with dense submergent or emergent aquatic vegetation. These tracts, which also demonstrated the greatest divergence between within-tract and control sediment MeHg:THg ratios, occurred throughout a wide area of the central through western Delta. Tracts with dense emergent tule (*Scirpus*) thickets and those with dense submergent *Egeria* patches both exhibited this pattern. In contrast, but consistent with the sediment MeHg spatial patterns, sediment MeHg:THg ratios within flooded tracts were absolutely lowest and were most similar to adjacent control sediments at tracts dominated by sand or mudflat habitat, such as the North Delta tracts and Mildred Island.

Figure 5(a-d) plots the relationships between sediment THg, MeHg, and organic percentage (as measured by loss on ignition, LOI) for the Delta samples analyzed in the Fall 2000 inside/outside tract study. General positive relationships were found between these parameters, with linear r^2 values of 0.37 between THg and MeHg ($p < 0.001$) and 0.30 between sediment organic percentage and THg ($p < 0.005$). The strongest relationship was found between sediment organic percentage and corresponding sediment MeHg ($r^2 = 0.65$, $p = 0.0001$). These patterns are consistent with the findings of Benoit *et al.* (1998) in the Patuxent River estuary. Krabbenhoft *et al.* (1999), in an extensive pilot study across the US of some of the factors potentially influencing sediment THg and MeHg concentrations, found a strong relationship between sediment THg and MeHg when both were first normalized to LOI ($r^2 = 0.86$). In our current study, no such relationship was apparent when all of the data were included (Figure 5d). However, two separate trends may be present in the LOI-normalized THg:MeHg relationship; a much steeper trend in MeHg vs THg from inside the highly vegetated Central and West Delta test tracts, as compared to North Delta tracts and various channel and slough habitats.

Sediment Methylation Potential Experiments

Initially, we attempted to directly quantify MeHg efflux from Delta sediments into overlying water. In laboratory core-tube experiments, we found that the changes in aqueous MeHg levels were too low for accurate measurement within our project constraints. Subsequently, we chose a sediment Hg-amendment technique which delivered well above detection results. Laboratory slurry experiments introduced spike additions of reactive inorganic Hg (aqueous mercury chloride) to Delta sediment samples and measured the MeHg production that resulted over 8-16 day periods. These measurements of “methylation potential” determine not what is naturally produced from a given sediment, but that sediment’s propensity to methylate inorganic Hg if it is presented in a bioavailable form under consistent laboratory conditions. The standard conditions utilized (1.00 ppm Hg spikes, temperature 22 °C, sparged with N₂ to anoxia) were not intended to represent either typical or maximal conditions for Delta sediment methylation. Indeed, sparging to anoxia may to some extent have inhibited methylation by promoting the accumulation of sulfides (e.g. Benoit *et al.* 1999). However, this slurry technique and others similar to it have proven useful as consistent rough benchmark measures of the relative potential of different sediments to methylate (and demethylate) Hg (e.g. Mack and Nelson 1997, Macalady *et al.* 2000).

Figure 6 displays time series methylation data from a representative experimental set. Following identical spike additions to 1.00 $\mu\text{g Hg g}^{-1}$, sediments from three different representative habitat types within the Cosumnes River portion of the Delta all reached a maximum MeHg balance within two days. Peak concentrations differed in the three representative sediments, though all rose well above initial levels. Methylmercury subsequently declined in the coarsest, mid-channel sample after day two. In the most organic-rich sediments, taken from a depositional, heavily-vegetated, off-channel marsh, MeHg persisted at maximal levels for six additional days beyond the initial rise. In the intermediate sediment, taken from a depositional (but not marsh) environment, peak levels persisted for an intermediate length of time (through day four). In all three sediments, following maximal initial MeHg concentrations,

levels maintained at approximately 50% of peak levels (well above baseline) for at least 8-16 days. The experimental declines from peak levels may be indicative of a demethylating phase.

The coarser, mid-channel sediments were also lowest in the absolute magnitude of the MeHg production peak (90 ng g^{-1} , vs a baseline of 10), intermediate in the off-channel depositional sediment (130 ng g^{-1} , vs a baseline of 20), and notably greatest in the organic-rich marsh sediment (390 ng g^{-1} , vs a baseline of 30). Figure 7 displays reduced data from this and other representative Delta marsh habitats and their respective adjacent non-marsh controls in units of peak MeHg concentrations during identical methylation potential experiments. Sediments from the lower Cosumnes River, Liberty Island in the North Delta, and Venice Cut Island in the Central Delta all demonstrated dramatically elevated levels of Hg methylation potential in the more organic-rich, heavily vegetated, flooded wetland sediments, relative to adjacent non-marsh controls. In the North Delta, while absolute levels were much lower, the difference in peak MeHg response to spike additions of inorganic Hg was 39 ng g^{-1} (marsh) and 2 ng g^{-1} (submerged island flats). It is notable that much of the North Delta is characterized by sandy sediments and turbid water that inhibit macrophyte development. Cosumnes region experimental concentrations, as noted above, were an order of magnitude greater at 399 ng g^{-1} (marsh) and 93 ng g^{-1} (channel). At Venice Cut Island, representative of peat-based Central through West Delta flooded tracts, the maximum MeHg concentration in spiked flooded peat material was 1077 ng g^{-1} , versus 34 ng g^{-1} in the adjacent control (submerged island flats). Similar patterns were found at other representative sites across the Delta. In all paired tests, flooded organic-rich wetland sediments exhibited between 2 and 30 times greater Hg methylation potential than adjacent channels and flats.

Aqueous Methylmercury Export vs Import From Flooded Wetland Tracts

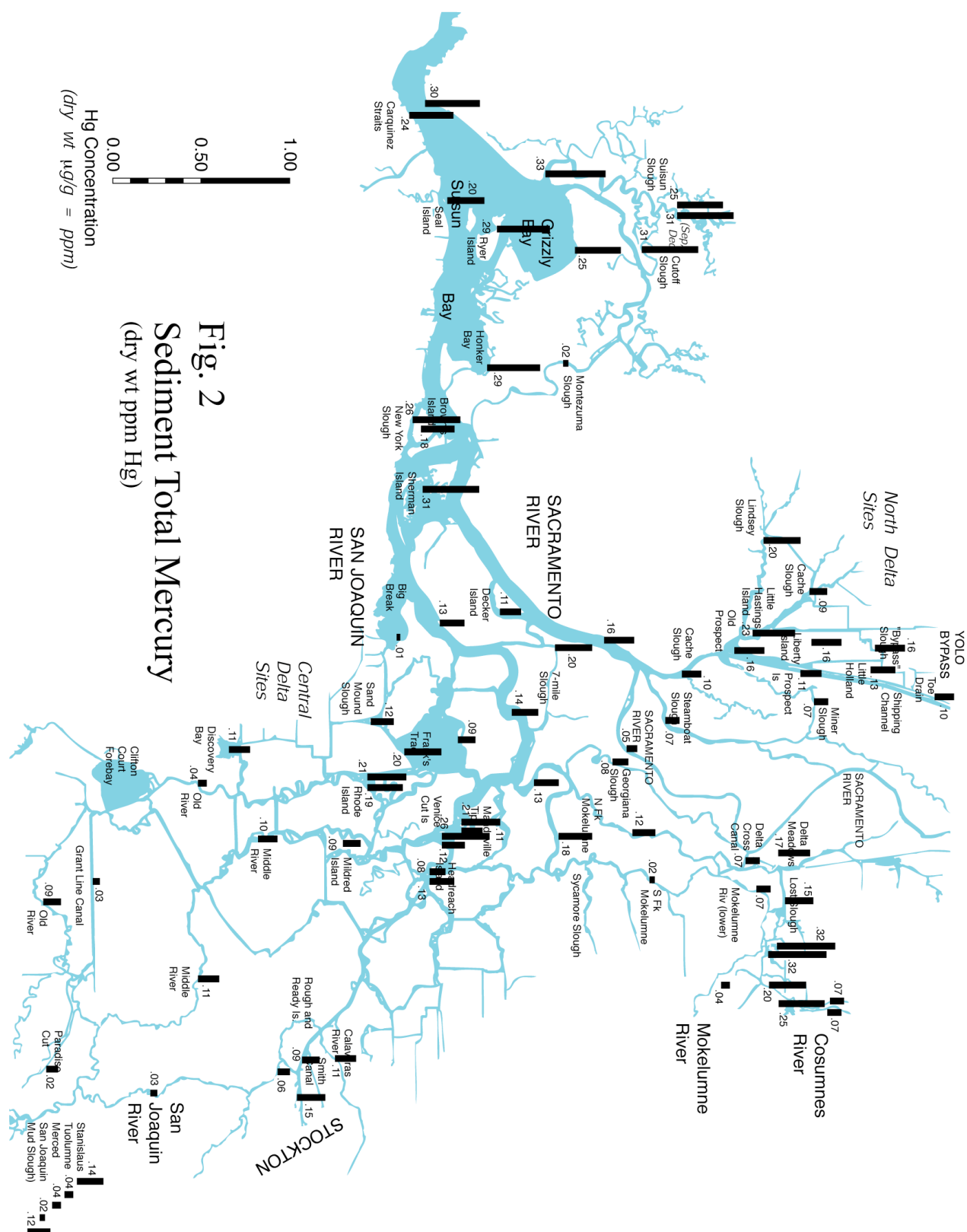
We directly tested a diverse set of flooded Delta tracts for potential net export of aqueous MeHg. This was done with a series of tidal water collections, in which we sampled inflowing and subsequent outflowing tidal Delta waters during high amplitude tidal cycles. Samples representing initial/inflowing water were taken toward the end of inflowing (rising tide) cycles at prominent breaches of the targeted flooded tracts. Corresponding samples representing export from the flooded tracts were taken at the same locations toward the end of the subsequent outflowing (lowering tide) cycle. Standard clean sampling protocols were used for all collections. Because of recurring detection problems with filtered aqueous MeHg in the Delta (reported by other CALFED researchers), we tested an alternate approach, utilizing raw aqueous MeHg (preserved/fixed same day with ultra-clean hydrochloric acid) in conjunction with corresponding samples of total suspended solids (TSS).

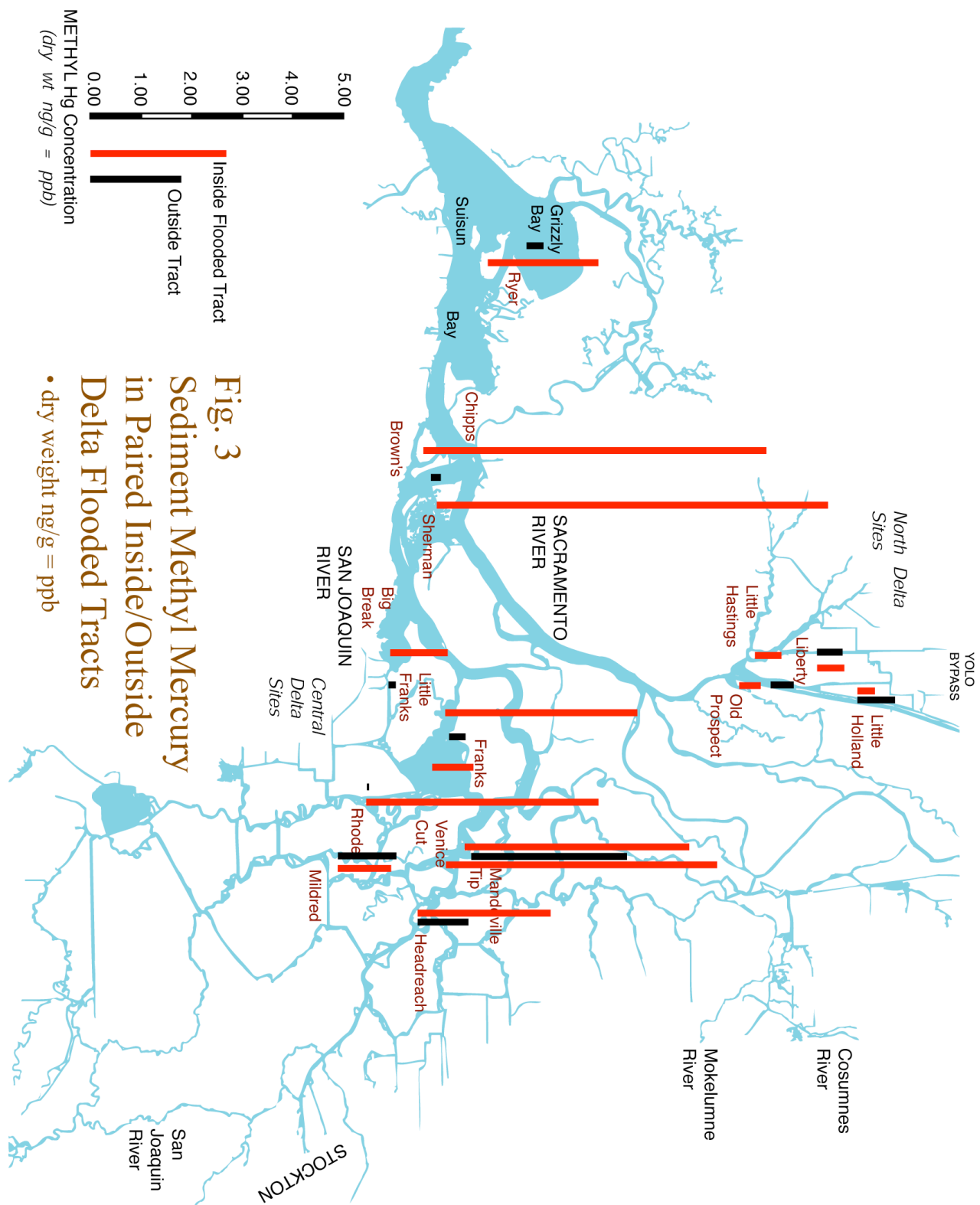
In Figure 8, absolute concentrations of raw aqueous MeHg are plotted for inflowing vs outflowing tidal water at eight important flooded Delta tracts and two integrating channel regions. At two large North Delta tracts with distinctly different habitats at either end (Liberty Island and Little Holland Tract), inflowing and outflowing water samples were taken from both the sand flat southern ends and the well developed tule marshes at the northern ends. In nearly all sample pairs taken throughout the Delta, outflowing aqueous MeHg was elevated over concentrations in inflowing water. This data indicates that the flooded Delta tracts may function

as relative MeHg sources for their surrounding regions (and the Bay-Delta as a whole). In paired samplings from the North Delta export-integrating site at Lower Cache Slough, though reduced in absolute concentration relative to the flooded tracts, the MeHg level in outflowing water was double that of the inflowing tide. These elevations in export water MeHg could be partially or largely a function of tidal flushing and associated sediment resuspension.

In Figure 9, the raw aqueous MeHg data have been normalized to corresponding suspended particulate concentrations. The data are plotted as ng aqueous MeHg per gram TSS. While strong relationships have been shown between TSS and total Hg in the Bay-Delta (Abu-Saba and Tang 2000), the association between MeHg and particulates is only recently being investigated for this system. In collaborative work by Foe *et al.* (this report), a positive relationship between TSS and aqueous MeHg was found at the X2 mixing zone of the West Delta ($p = 0.005$), with a positive but less strong relationship at Greene's Landing on the Sacramento River ($P < 0.03$). In our UC Davis 2001 flooded tract inflow/outflow study, a generally positive relationship was also found between TSS and aqueous MeHg, with a p of 0.0004 and an r^2 of 0.46.

By normalizing to TSS, we are not implying that all of the aqueous MeHg is associated with the corresponding particulates; we are simply factoring out the particulate load as the explanation for the variation in aqueous MeHg. Plotted in this way (Figure 9), the elevated MeHg in outflowing water at Lower Cache Slough in Figure 8 appears to be entirely a function of increased suspended solids in the outflowing water. The large mud/sand flat expanses of Liberty Island, Little Holland Tract, and Mildred Island demonstrated a net *decrease* in outflowing aqueous particulate MeHg concentration. However, in virtually all of the tested flooded tract sites characterized by dense aquatic plant growth and organic-rich sediments, aqueous particulate MeHg (concentration) was substantially elevated in outflowing vs inflowing tidal water. The most notable relative elevations in exported aqueous particulate MeHg concentrations occurred in the highly developed emergent tule (*Scirpus*) marsh habitat of representative site Mandeville Tip Island and the dense submergent *Egeria* macrophyte beds of representative Little Franks Tract. The marshy northern ends of the North Delta tracts were also found to export elevated concentration aqueous particulate MeHg, while the predominant mudflat and sandflat habitats there were not. This indicates that both types of flooded Delta tracts may function as relative exporters of aqueous MeHg to the wider Delta: turbid mudflat-dominated tracts characteristic of the North Delta through resuspension and export of low to moderate concentration sediment, and the organic-rich, vegetated wetlands through relatively highly elevated local production of MeHg and aqueous export of elevated concentrations per exported particulate unit. We have noted in our field observations that the North Delta type of sandflat/mudflat-dominated tracts appeared to often export water that was elevated in suspended solids relative to inflow water, thus frequently functioning as net erosional zones. In contrast, flooded tracts containing dense emergent or submergent marsh vegetation were noted to often export substantially clearer water relative to inflows. Flats-type tracts may provide net export of low-moderate MeHg concentration particulates, while vegetated, flooded Delta tracts may function as net traps for particulates and THg, while simultaneously functioning as net sources of MeHg. This would be consistent with the findings of Mason *et al.* (1999) in the Chesapeake Bay estuary, as well as with general reports of flooded wetland habitats functioning as net sources of MeHg (e.g. St. Louis *et al.* 1994, Hurley *et al.* 1995, Krabbenhoft *et al.* 1999).





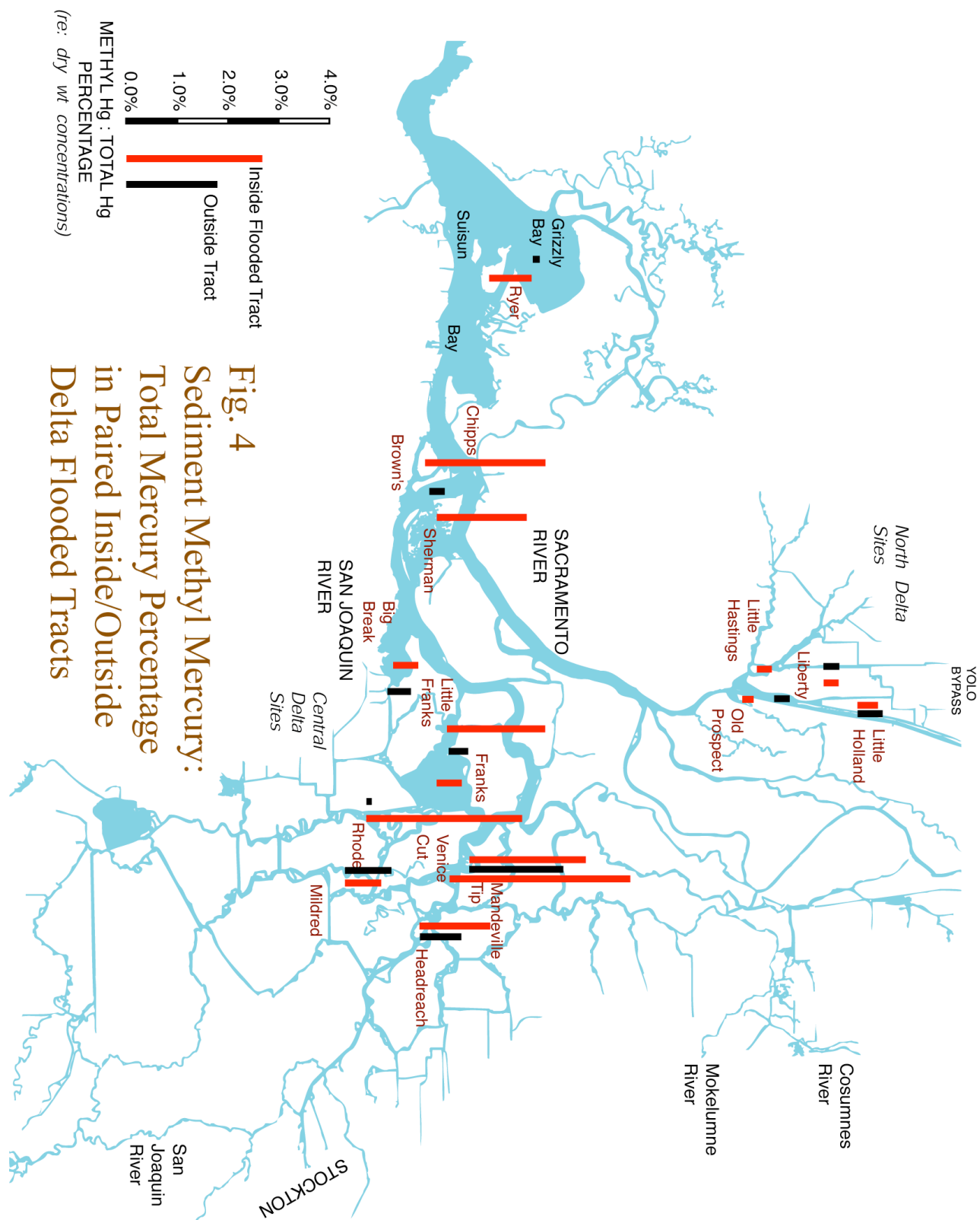


Fig. 4
Sediment Methyl Mercury:
Total Mercury Percentage
in Paired Inside/Outside
Delta Flooded Tracts

Fig. 5(a-b)

Sediment organic matter percentage (as measured by Loss on Ignition, LOI) vs. sediment THg and MeHg for paired inside/outside Delta flooded tract samples. (Samples collected Sep. 2000)

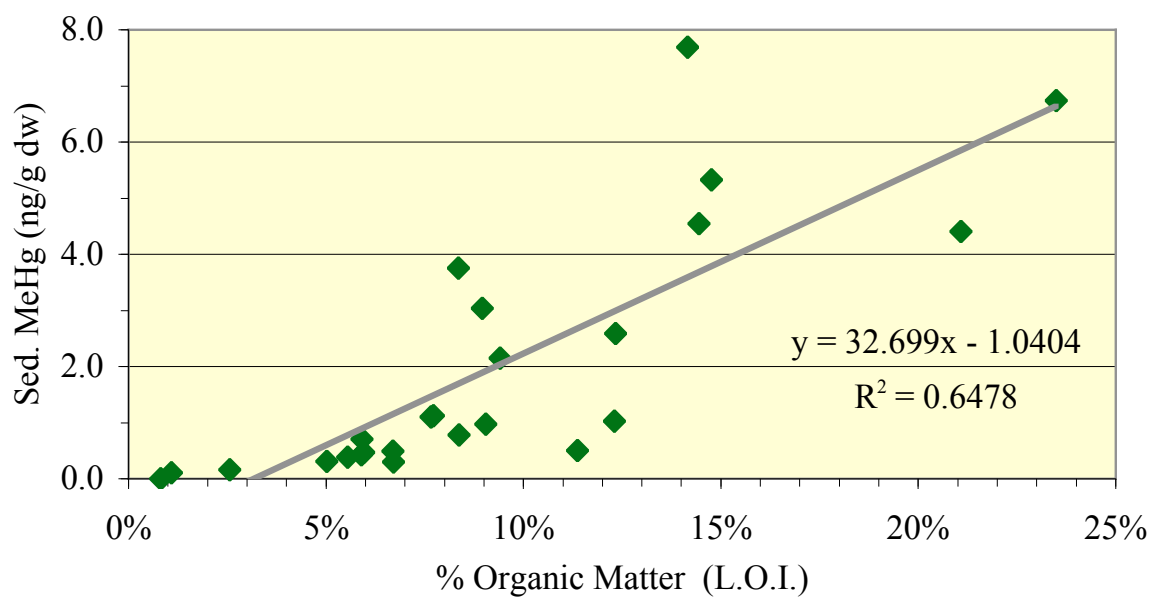
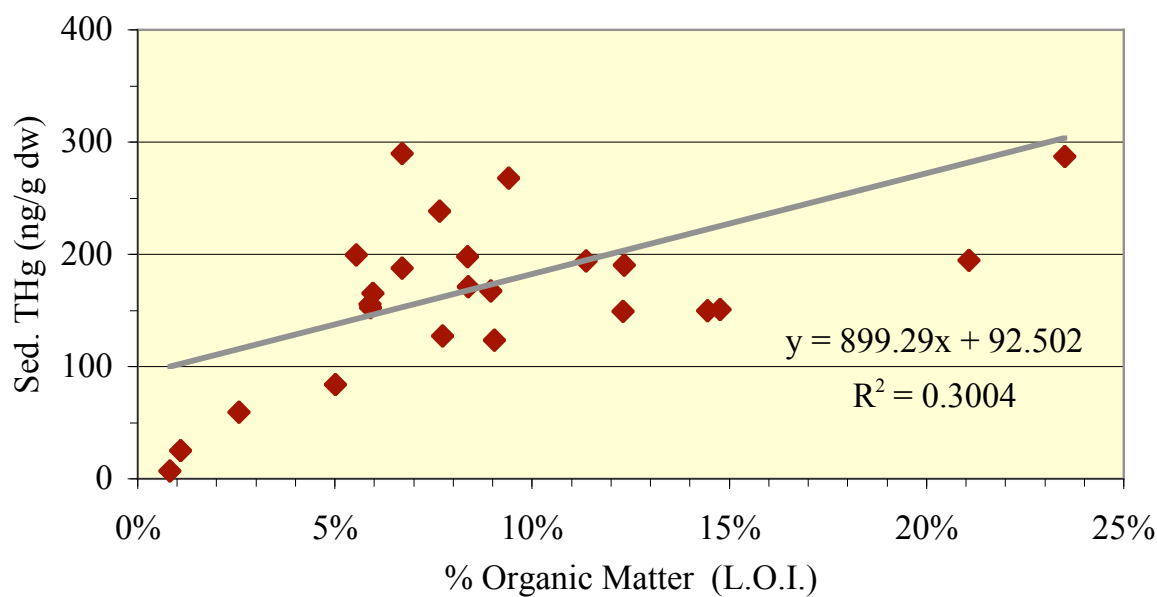


Fig. 5(c-d).

Sediment THg vs. MeHg and sediment THg normalized to LOI vs. MeHg normalized to LOI, for paired inside/outside Delta flooded tract samples.
(Samples collected Sep. 2000)

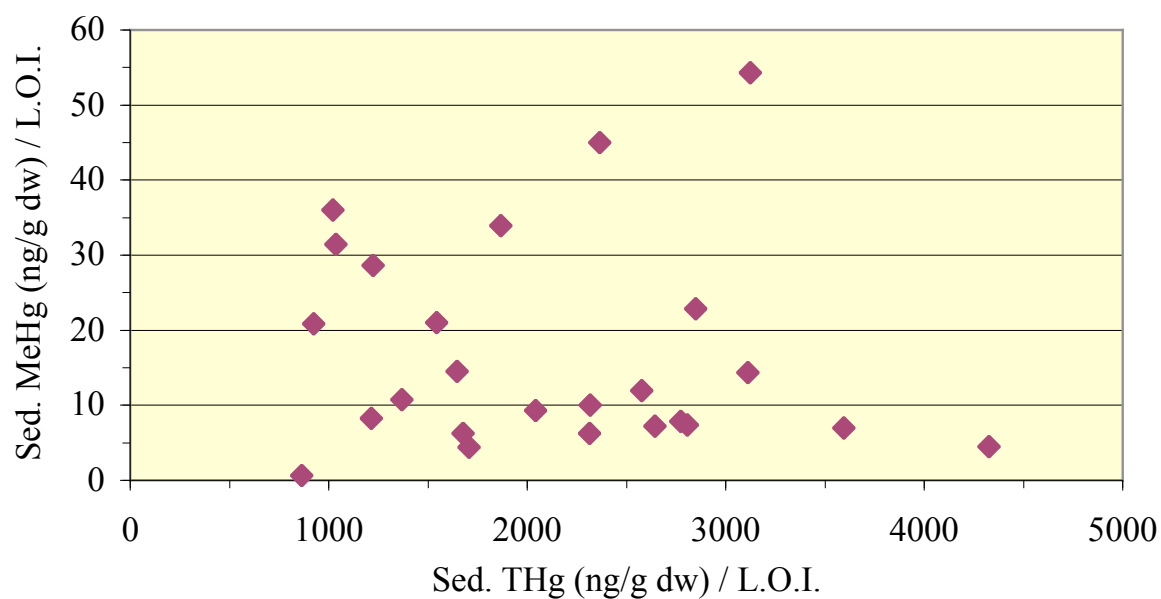
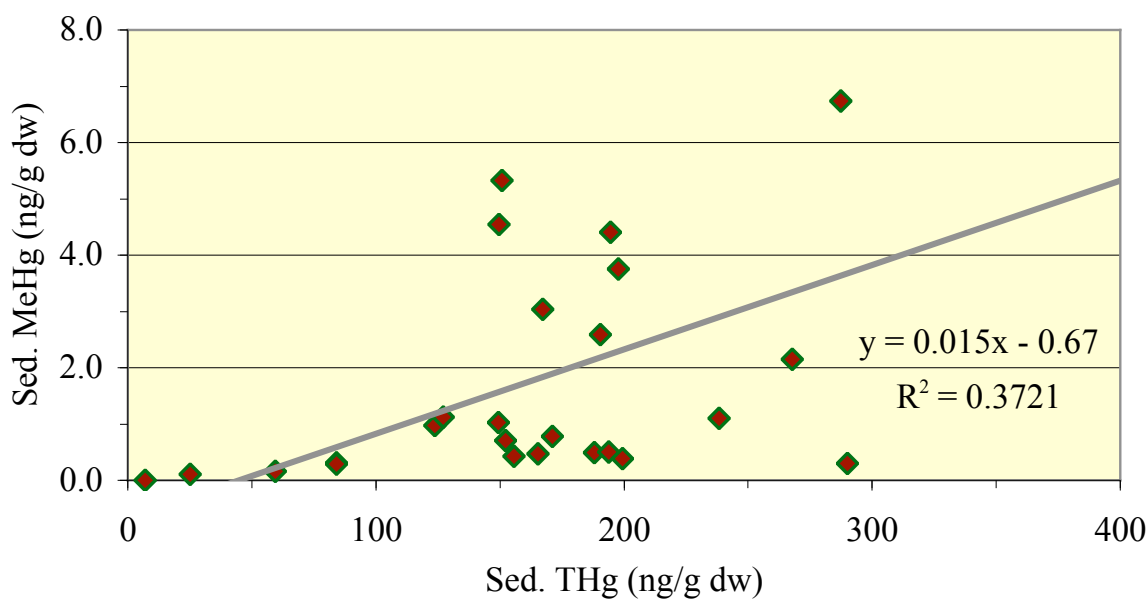


Fig. 6

Time course of net methylmercury concentrations in spiked laboratory sediment incubations.
(*Cosumnes region sediments with inorganic Hg added to 1.00 ppm*)

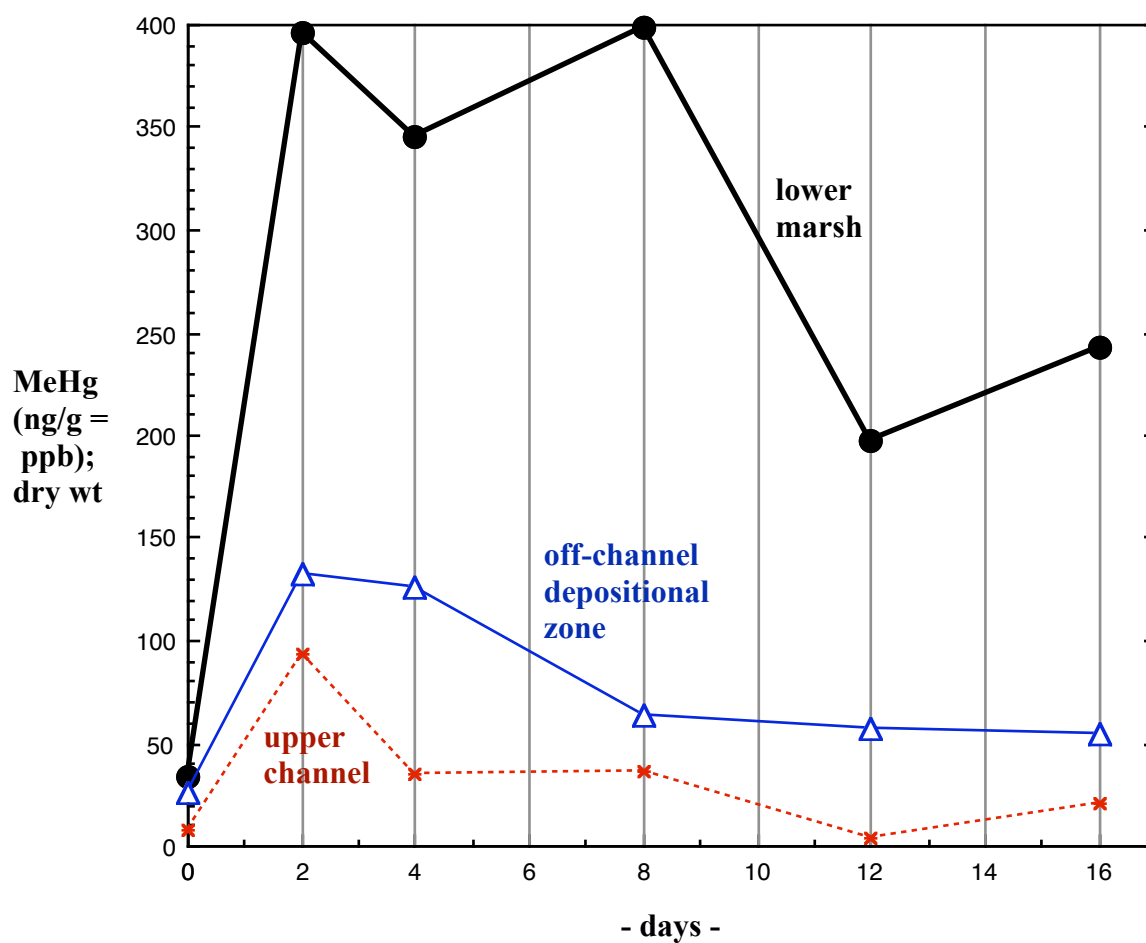


Fig. 7**Relative mercury methylation potential of representative Delta marsh habitats vs adjacent aquatic habitat.**

(Mean maximum methyl mercury concentrations in inorganic mercury addition experiments to $1.00 \mu\text{g Hg g}^{-1}$; methylmercury concentrations in dry wt $\text{ng Hg g}^{-1} = \text{ppb}$).

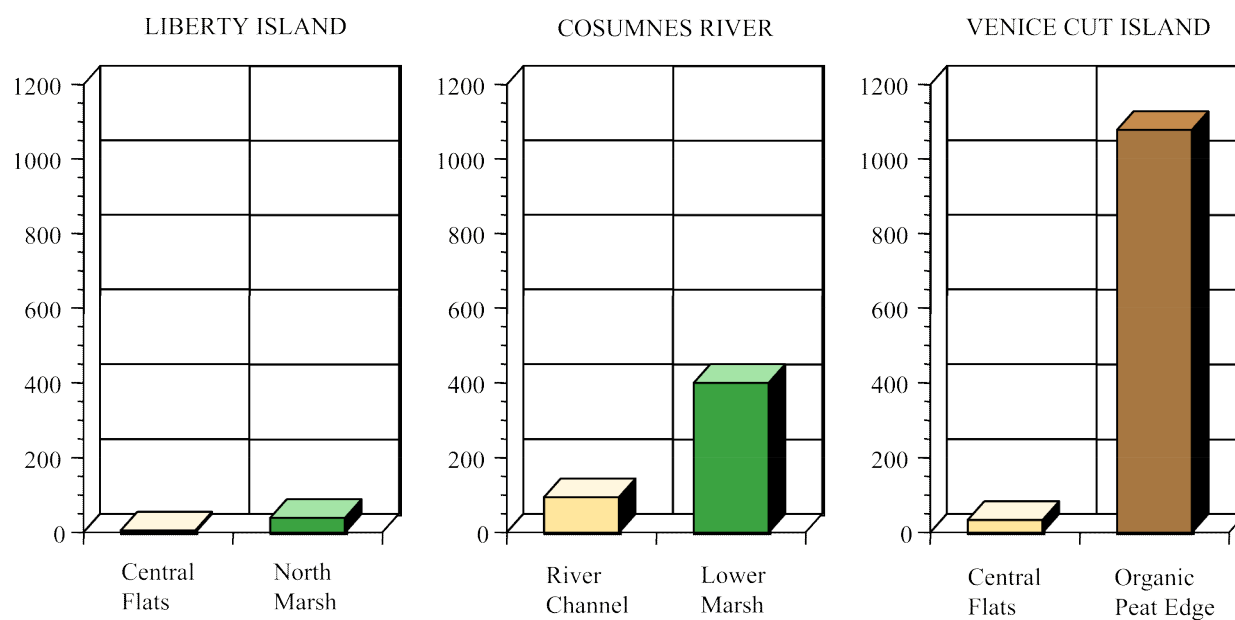


Fig. 8
Aqueous Methyl Mercury
in Paired Inflowing vs
Outflowing Tidal Water in
Delta Flooded Tracts
(June 2001)

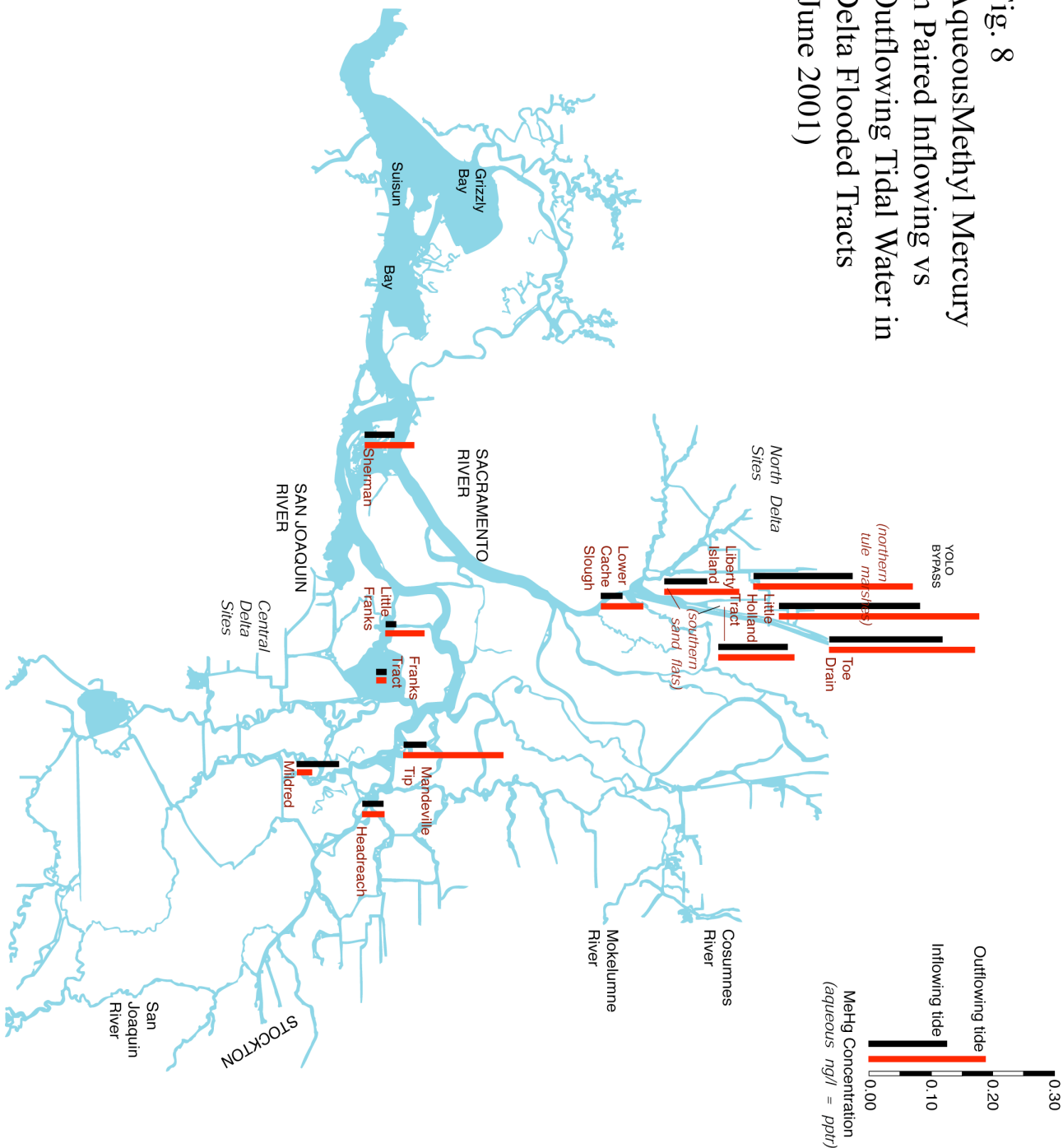
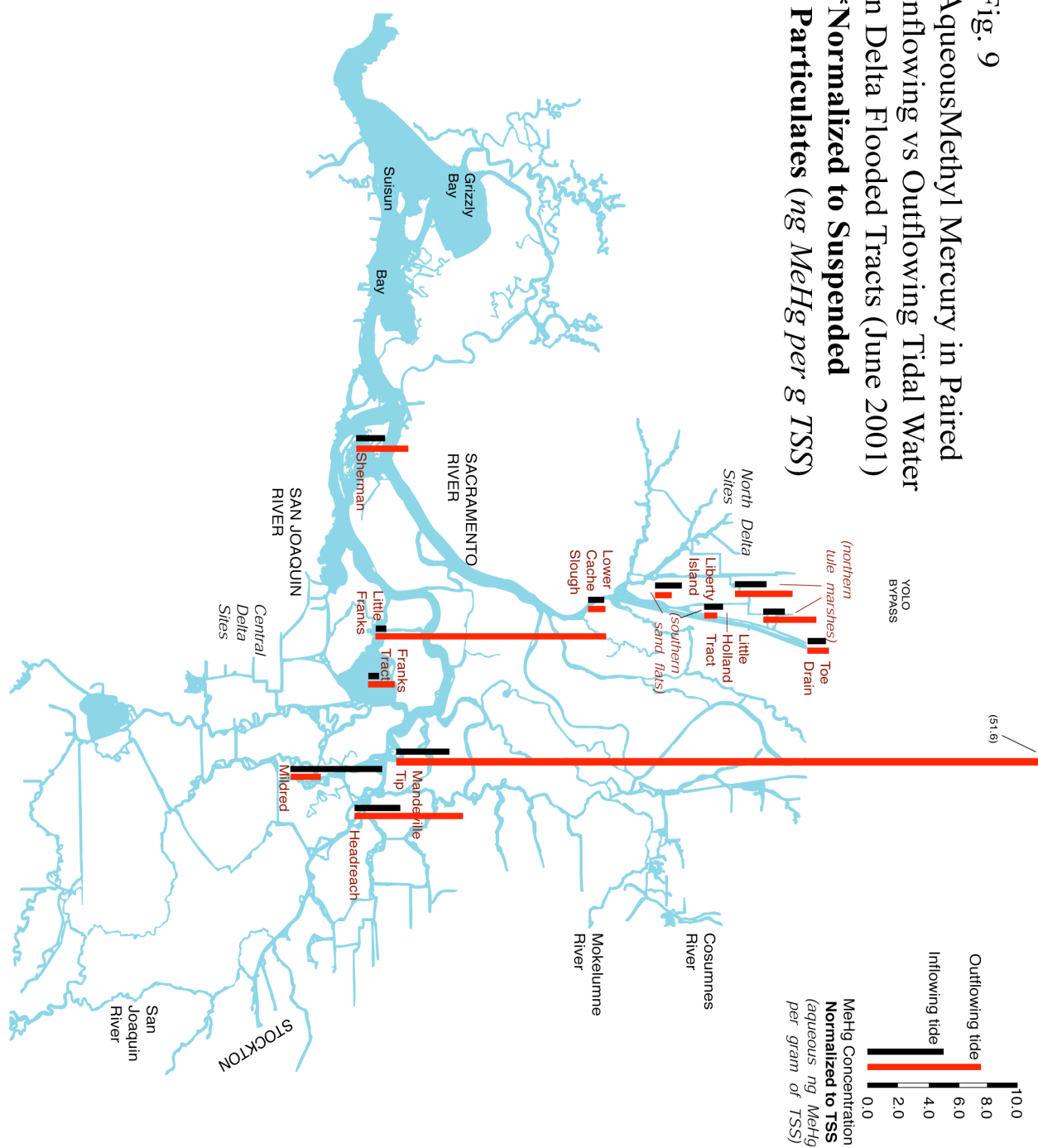


Fig. 9
Aqueous Methyl Mercury in Paired
Inflowing vs Outflowing Tidal Water
in Delta Flooded Tracts (June 2001)
***Normalized to Suspended**
Particulates (ng MeHg per g TSS)



Biotic Indicators of Relative Mercury Exposure Throughout the Delta

Choosing appropriate bioindicator species

One objective of this initial study was to utilize naturally occurring aquatic organisms as indicators of relative MeHg exposure and bioaccumulation across the system. Ideally, we wanted organisms which (1) exhibited relative site fidelity, (2) could be taken from a wide variety of Delta locations and habitats, (3) were probable consumption targets of other wildlife, (4) had relatively predictable trophic status, and (5) had the ability to uptake MeHg relative to exposure. In the initial rounds of field sampling, we found that many otherwise appropriate small fish and macro-invertebrate species had limited spatial ranges throughout the Delta. While these may be useful bioindicators of local food web dynamics and can provide corroborating evidence of Hg exposure trends, they were not felt to be adequate for Delta-wide comparisons. We found the invertebrates Asiatic clams (*Corbicula fluminea*) and signal crayfish (*Pacifastacus leniusculus*) and the small fish inland silversides (*Menidia beryllina*) to have the most extensive combinations of favorable characteristics for potential use as bioindicators throughout the Delta, including adequate spatial distributions and relative abundances.

Asiatic clams (*Corbicula fluminea*) are a widely distributed non-native filter feeder. Although their importance as a food item is rather limited, they are consumed by certain species of Delta wildlife and by some people. Inza et al. (1997, 1998) have extensively studied the Hg uptake and depuration dynamics of this species, finding that MeHg uptake rapidly increased with exposure time without reaching saturation. Depuration of MeHg was found to be relatively slow in that research, with a 40% loss over a 120 day period. The ability to uptake MeHg relative to exposure, wide distribution, relative ease of collection, and consistency of trophic status made *Corbicula* a strong choice as a potential bioindicator of Delta-wide relative MeHg exposure and bioaccumulation. As this species is an obligate phytoplanktivore, we additionally hoped to use it as a consistent “trophic baseline” in stable isotopic investigations of relative trophic level in co-occurring organisms.

Native signal crayfish (*Pacifastacus leniusculus*) are common throughout the flowing, freshwater channels of the Delta. Headon et al. (1996) reported that crayfish efficiently assimilate and biomagnify MeHg from their food, with little depuration. Simon and others (2000) found that, in crayfish, MeHg bioaccumulates most efficiently into the green gland and tail muscle, providing a direct route for transfer to predators, including humans. Crayfish are commercially fished in the Delta for human consumption and are regularly consumed by fish, birds, and mammals such as otters and mink. However, as a bioindicator they are relatively difficult to sample (generally requiring multiple day sampling with overnight trapping), their trophic status is not consistent, and their long lifespan may complicate assessment of exposure period.

Inland silversides (*Menidia beryllina*) are short lived, introduced, schooling, planktivorous fish that are highly abundant and widely distributed in the Delta, particularly in shallow waters. Due to their abundance and habitat preference, silversides are likely a common food item for piscivorous fish and birds in the Delta. Fish are the most frequently used bioindicators of Hg contamination; bioaccumulation and slow depuration of MeHg in fish has

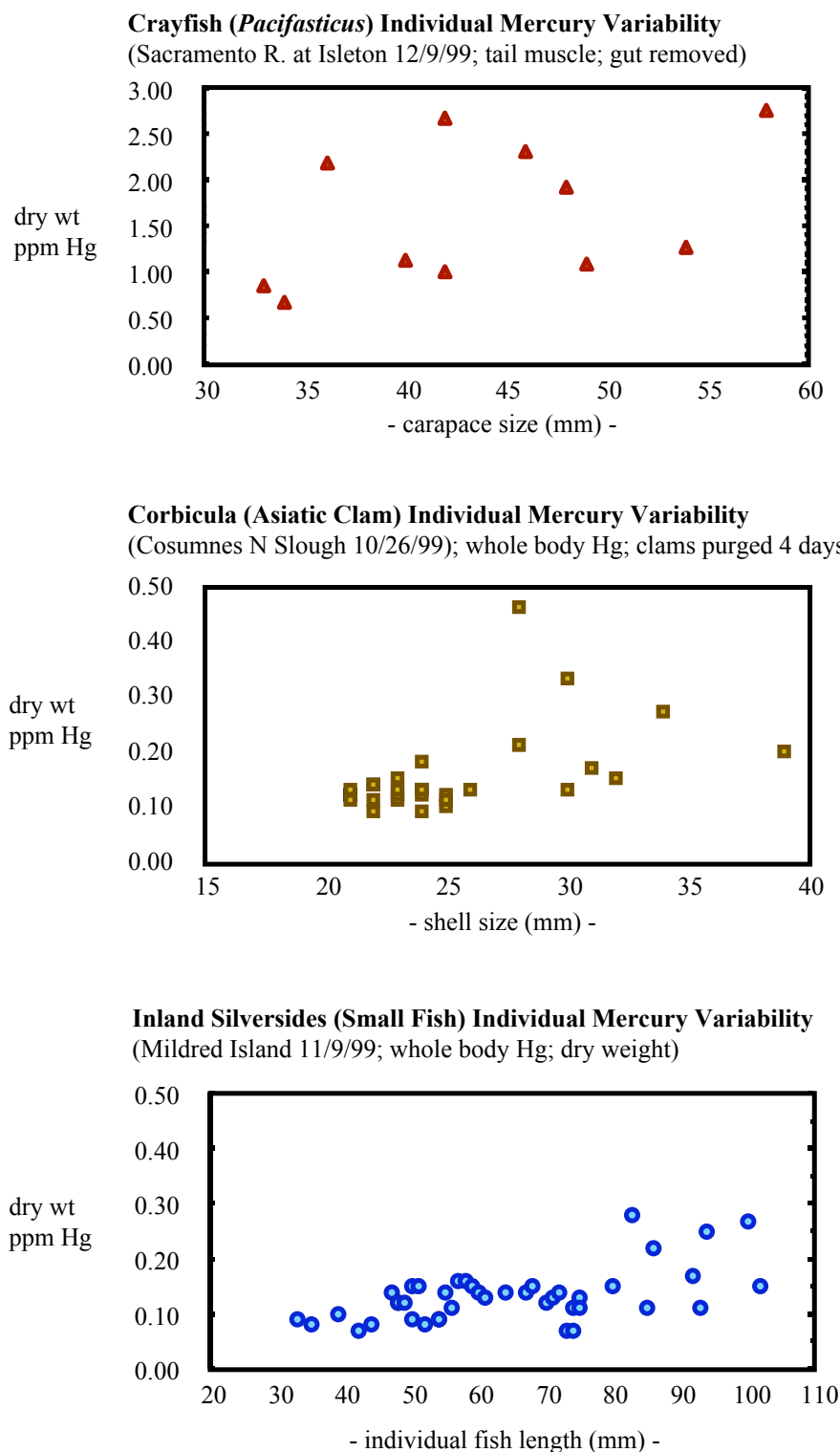
been well documented (US EPA 2001). In silversides, the short lifespan could help to define the period of Hg exposure, making them a prospective bioindicator for the measurement of inter-annual and seasonal variability. Silversides trophic level variability is limited by the size of the items they can ingest. Trophic status may be complicated somewhat by a partial diet switch, among larger individuals, from zooplankton to larval fish at certain times of the year.

Asiatic clams, signal crayfish, and inland silversides were investigated as primary Hg bioindicators in the Delta. Additional samples were taken as available of taxa that were locally abundant and important in local food webs. An initial research focus was the study of individual variation in Hg levels within each of the various biotic sample types, from identical locales. In order to be most useful in describing potential spatial and inter-habitat variation in Delta Hg bioavailability, low levels of within-site variation were needed in the monitoring organisms. In Figure 10, typical within-site Hg variability in individuals of each of the three primary candidate types of biota is displayed in size versus Hg plots.

Native signal crayfish (*Pacifasticus leniusculus*) were typically found to have unacceptably high levels of within-site variability in tail muscle Hg concentration. This was likely a function of a highly variable, opportunistic diet and the co-occurrence of widely varying age classes. Individual variability was frequently equal to or greater than the spatial and habitat related Hg variability. There was no apparent size range that was free of this high variability. This was unfortunate as, otherwise, crayfish could be ideal candidates as bioindicator species. They were found to accumulate Hg to high concentrations, similar to predatory fish, while maintaining relatively localized home ranges.

Asiatic clams (*Corbicula fluminea*) demonstrated very low individual Hg variability in the smaller size classes, from most locations investigated. Individuals less than 28 mm in size (maximum shell diameter) were quite consistent in purged, whole body Hg concentration. Above this size at a number of sites tested, individual variability increased significantly. We attributed this to age structure and sexual maturity. Larger fall clams demonstrated a significant variation in body mass, likely a function of reproductive energy needs and spawning. Individuals which metabolized much of their body mass were left with similar Hg body burdens but elevated concentrations. Based on these findings, we chose 15-27 mm *Corbicula* as one of our two primary Delta-wide Hg bioindicators.

Inland silversides (*Menidia beryllina*) were found to behave primarily as annual fish in the Delta, as is the case in most other parts of the state where they are prevalent. Fall silversides were typically very consistent in same-site, individual, whole body Hg concentration at sizes of ca. 45-75 mm. Above this size, individual Hg concentrations were often significantly more variable. Our interpretation, supported by field observation of Delta silverside life history, is that fall individuals below approximately 75 mm are the young-of-year class. Larger individuals consist primarily of over-wintering fish from the previous year. We chose 45-75 mm silversides as our second primary Delta-wide Hg bioindicator.

Fig. 10**Examples of individual variability in mercury content among potential bioindicators.***(individual dry wt $\mu\text{g/g}$ Hg = ppm, plotted as a function of organism size/age)**(dry wt concentrations = app. 5x wet wt concentrations)*

Mercury in clams (Corbicula fluminea, Figures 11 and 12)

Figures 11 and 12 show Hg concentrations in 15-27 mm *Corbicula* from multi-individual, whole body composites taken consistently at diverse sites throughout the Delta. Inorganic Hg and MeHg:THg ratios were highly variable in the bivalves (Figure 11). One of the most notable features of the *Corbicula* THg data set was the presence of the highest overall concentrations at west Delta sites between Ryer Island to the west and Big Break, Gallagher Slough, and Sand Mound Slough to the east. Throughout this region, *Corbicula* THg concentrations were between 0.32 and 1.08 $\mu\text{g g}^{-1}$ (dry weight). Composites of another bivalve, *Potamocorbula amurensis*, taken at the upstream side of Carquinez Strait, were also relatively elevated in THg (0.37-0.42 $\mu\text{g g}^{-1}$). Suisun Slough and Grizzly Bay (0.15-0.26 $\mu\text{g g}^{-1}$) did not appear to be the source of elevated West Delta THg bioaccumulation. Relatively elevated THg was also seen in relation to several tributary sites such as the Cosumnes River. However, these spikes in THg, particularly throughout the west Delta, were not accompanied by proportional elevations in MeHg.

In contrast with the variable spatial trends in clam THg and, particularly, THg:MeHg ratio, the spatial trend for *Corbicula* MeHg demonstrated relatively smooth gradations from site to site and region to region (Figure 12). Greatest levels of clam MeHg occurred at the periphery of the Delta, at the mouths of inflowing tributaries, particularly the Cosumnes River in the east Delta and the Stanislaus River in the south Delta. Moderately elevated MeHg occurred downstream of the Cosumnes/Mokelumne inflows, in the North Delta and Sacramento River, and downstream of the North Delta/Sacramento River into the West Delta. One of the most notable features of the *Corbicula* MeHg data set was the presence of consistently lowest concentrations throughout a wide region of the southern and central Delta. This region, as noted previously, contained numerous wetland tracts in advanced stages of vegetative succession, where net sediment Hg methylation and export could be expected to be elevated. This apparent contradiction between sediment methylation processes and bioaccumulation may represent a contrast with results from a large, multi-investigator study in the northern Florida Everglades. In that study, Gilmour et al. (1998) found relative bioaccumulation to be associated with corresponding sediment MeHg concentrations and methylation rates.

Throughout the entire Delta, there was no indication of localized increases in *Corbicula* Hg concentrations as a function of micro-habitat. Clams from flooded wetland tracts consistently exhibited Hg levels that were similar to those from control sites within the same sub-region. In paired collections (inside/outside flooded tracts) from Venice Cut and Rhode Islands, concentrations were statistically indistinguishable.

Mercury in inland silversides (Menidia beryllina, Figures 13 and 14)

Figure 13 displays inland silverside methyl and total Hg from 45-75 mm, multi-individual, whole body composites taken at 64 sites throughout the Delta in the fall of 1999. These small, schooling fish accumulate their Hg over a larger region than the clams, likely integrating across each individual flooded tract or slough where collected and, thus, being more representative of average Hg conditions at each site. As a result, the silverside data set grades

very evenly from site to adjacent site and provides perhaps the best broad spatial measure to date of relative Hg bioavailability to fishes throughout the Delta. Additionally, Hg in silversides whole fish composites was found to consist essentially entirely of MeHg ($103\% \pm 17\%$ of THg in 64 paired analyses; Figure 13). In Figure 14, silversides THg is plotted alone; QA/QC for THg was tighter than that for MeHg.

Mercury concentrations in silversides were consistently elevated in the Cosumnes and Mokelumne Rivers ($0.30\text{--}0.55 \mu\text{g g}^{-1}$) and the North Delta sites exposed to Yolo Bypass flows ($0.18\text{--}0.46 \mu\text{g g}^{-1}$), with highest regional levels closest to the undiluted inflows. Elevated to a lesser extent were the channels carrying Sacramento River water (Sacramento River, Steamboat and Georgiana Sloughs, Delta Cross Canal), which were very similar in silversides Hg at $0.21\text{--}0.28 \mu\text{g g}^{-1}$. Collections in the target size class were not possible in the Stanislaus, Tuolumne, or Merced Rivers, but composites from the San Joaquin River upstream of the Merced ($0.79 \mu\text{g g}^{-1}$) and from Mud Slough at Kesterson Reserve ($0.69 \mu\text{g g}^{-1}$) contained the highest silversides Hg of the survey. However, as in the clams, this did not translate into elevated levels downstream in the South Delta. Silversides from the entire South and Central portions of the Delta were uniformly low in Hg ($0.08\text{--}0.19 \mu\text{g g}^{-1}$) relative to concentrations from the tributary regions. Samples from west of the Sacramento-San Joaquin confluence to the Carquinez Strait exhibited elevated levels similar to those of the northern and eastern inflow regions, at $0.21\text{--}0.38 \mu\text{g g}^{-1}$. The West Delta showed a distinct signal of increased Hg bioaccumulation relative to the Central Delta and adjacent sites between the West Delta and tributary inflow regions. Consistent with the clam record, the South and Central Delta demonstrated the lowest levels of silversides Hg bioaccumulation in the entire system.

Also as seen in the clam MeHg data, silversides demonstrated little or no localized elevation in MeHg concentrations in relation to flooded wetland habitats. Fish from large, relatively isolated flooded tracts in the North Delta such as Liberty Island ($0.29 \mu\text{g g}^{-1}$) and Little Holland Tract ($0.18 \mu\text{g g}^{-1}$) were not elevated over control samples from adjacent and regional channel/slough sites ($0.21\text{--}0.46 \mu\text{g g}^{-1}$). The Central Delta, with its prevalence of flooded marshland tracts, also showed no relative increase in silverside Hg concentration in flooded tracts vs control sites, with all concentrations throughout the region being uniformly low relative to tributary inflow sites and the West Delta.

Inter-Annual Variability in Silversides Hg Bioaccumulation (Figure 15)

Figure 15 displays Hg levels in inland silversides composite samples taken in three different years: 1998, 1999, and 2000. Sampling was conducted at a similar time each year in the fall, when this largely annual species reached target sampling size (45–75 mm) and had incorporated Hg bioaccumulated throughout the warm season. While this is a limited data set and we were not able to obtain samples from all comparative sites in each of the three years, several points can be made.

The data from this representative forage fish species indicate the potential for substantial inter-annual variability in relative Hg bioaccumulation. Silversides Hg bioaccumulation in 1998 was elevated relative to 1999 and 2000 across most of the system. This trend was most

pronounced at sites closest to tributary inflows, including the Cosumnes River (+96% vs 1999), the North Delta (+89%), and the San Joaquin River (+64%). A more muted, but still notable relative elevation was apparent in 1998 vs 1999 at Mildred Island in the Central Delta (+25%) and Grizzly Bay in the West Delta (+37%). Among the sampling sites for which data were available in all three years, only the site at the back of Suisun Slough exhibited relatively static silversides Hg. We note that this site is hydrologically removed from sediment inputs to the Delta from the primary tributaries. These data are consistent with the hypothesis that ongoing inflows of tributary-derived Hg are an important driver of Hg bioaccumulation patterns in the overall system. They also demonstrate that the bioindicator organisms can respond to inter-annual changes (presumably in MeHg exposure levels).

The relative elevation of the 1998 Hg bioaccumulation data is interesting. We note that the most significantly elevated tributary runoff in the Bay-Delta watershed in recent years occurred in 1997. We have no samples from that year, but suspect that the elevated Delta Hg bioaccumulation of 1998 was residually related to tributary inputs from the high-energy 1997 events. It is notable that Davis *et al.* (this report) found substantially elevated Hg in largemouth bass, across the system, in the first year of their study (1999) as compared to the second (2000). We hypothesize that this 1999 elevation in bass Hg was related to ingestion of elevated Hg forage fish in the previous year(s) and that the large fish demonstrate temporal Hg trends that are muted and delayed, relative to shorter-lived, lower trophic level bioindicators.

In addition to inter-annual variability in biotic Hg concentrations, we noted over the course of the study that intra-annual (seasonal) shifts could be important, sufficient to potentially alter data interpretation if not taken into account. In particular, *Corbicula* were found to be relatively elevated in Hg in the spring, while inland silversides were found to be relatively elevated in the fall. We would encourage future monitoring efforts to further examine these apparent patterns and design routine sampling plans accordingly.

Stable isotopes and food web considerations

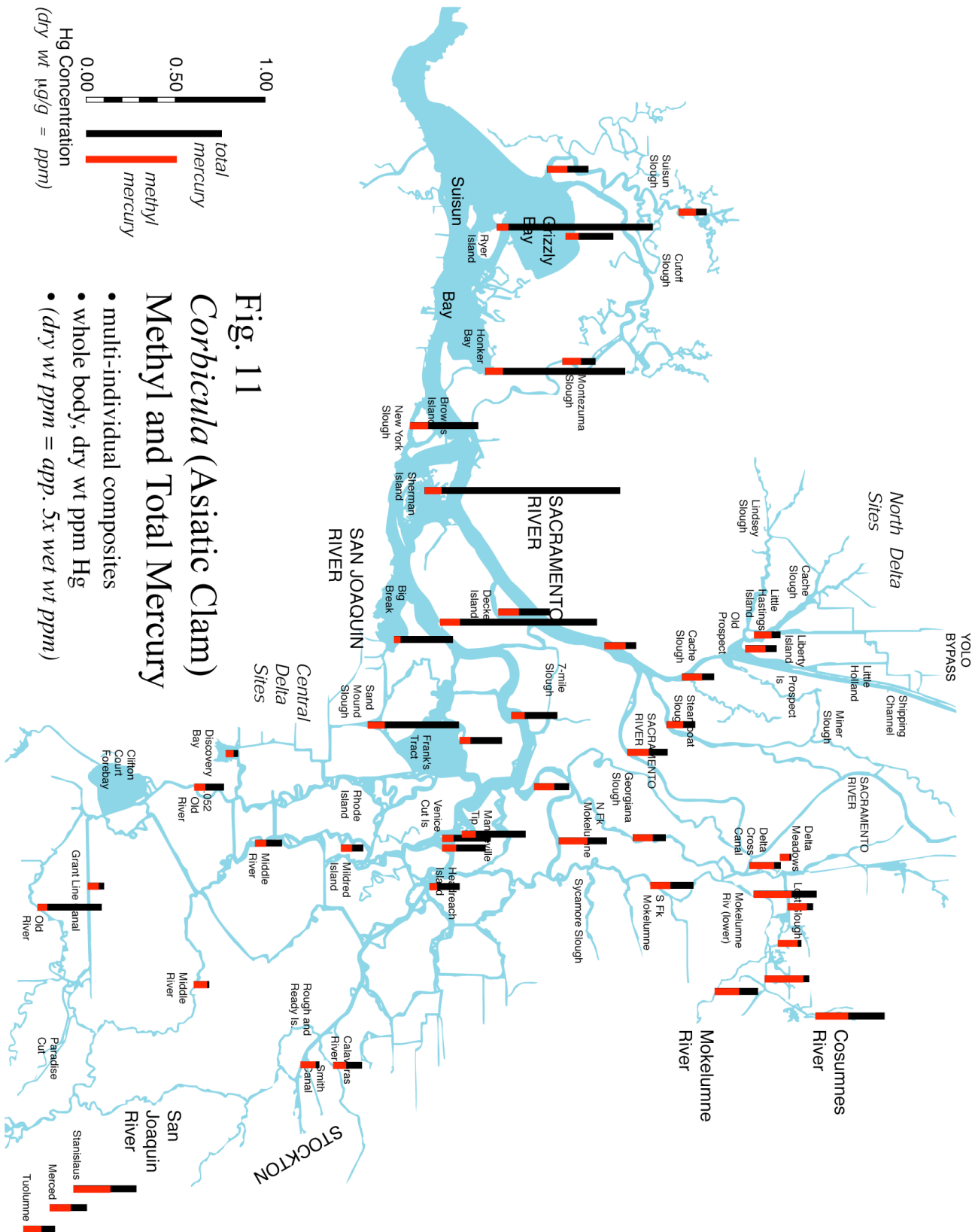
Nitrogen and carbon stable isotopic ratios were investigated in the biotic Delta samples in a preliminary attempt to account for potential variability in food web complexity between sites and regions. Relative differences in the number of primary food web links can potentially have a significant influence on ultimate localized Hg bioaccumulation in upper trophic levels (e.g. Bowles *et al.* 2001). We wanted to account for this potential variable in relation to observed spatial and temporal differences in Hg bioaccumulation. We recognized in advance the difficulties inherent to food web studies in a system as complex as the Sacramento-San Joaquin Delta (e.g. Cleckner *et al.*) and were not overly surprised to find the isotopic results from our limited sampling to be difficult or impossible to interpret. The ratio of nitrogen isotopes is utilized in the determination of relative trophic level. However, samples being thus compared must also be demonstrated to reside along the same basic food chain. Isotopic ratios of carbon are utilized to establish this linkage. The Delta biotic isotope samples were confounded in two major ways. First, different base carbon signatures were observed among the primary tributary inflow regions (i.e. Sacramento River vs East Delta tributaries) and between the tributaries and the Central and West Delta. Secondly, the carbon signature from *Corbicula* (Asiatic clams) was

found to apparently exist along a different trophic pathway than any of the other invertebrate or small fish bioindicator species utilized in the study. This unexpected result largely nullified our study design plan to utilize *Corbicula* as a primary consumer baseline in site-specific corrections of nitrogen isotopic ratios for the other bioindicators. We are continuing to examine these data and may present them at the September meetings and/or in potential future revisions of this document. In any case, these preliminary results will be useful precursors to future studies of food web structure in this complex system.

Spatial Hg Bioaccumulation Trends in Additional Indicator Organisms (Figures 16-25)

While the secondary bioindicator species sampled in this project exhibited more limited spatial distributions than the primary target organisms, the results from these samples can be compared and contrasted with the findings from the primary indicators across the areas of overlap. Map figures displaying relative Hg concentrations for each of the secondary indicator species are displayed in Figures 16-25. Five to ten samples of each of the secondary indicator species were analyzed for MeHg in addition to THg. High methyl:total ratios of 75-100+% were found in all. Because of the difficulties encountered in the interpretation of stable isotope results, these Hg data from additional Delta biota could provide important additional support for the distributional patterns in Hg bioaccumulation described by the clam and silversides data sets. Virtually all of the additional species demonstrated Hg bioaccumulation spatial patterns that were consistent with the trends indicated by the primary indicator species. Across a variety of small fish (plus signal crayfish), greatest intra-species Hg bioaccumulation levels were generally present near the previously identified tributary inflows and lowest levels were seen throughout the same region of the South and Central Delta. Distributions were sufficient to generally support this pattern in signal crayfish (Figure 16), threadfin shad (Figure 17), juvenile largemouth bass (Figure 18), juvenile bluegill sunfish (Figure 19), mosquitofish (Figure 20), and yellowfin goby (Figure 21). Data from the remaining four species occurred across too limited of a spatial range for comparison, but were also not inconsistent with these patterns.

The consistency of these general spatial Hg bioaccumulation patterns across many different biota, of varying trophic status, further indicates that these trends are real and representative of relative biological MeHg exposure and accumulation levels across the system. Additionally, all are supportive of the results of Davis et al. (this report) for game fish Hg distribution across the Delta region, particularly largemouth bass. It is notable that the lower trophic level species sampled and analyzed by UC Davis (including the frequently dominant inland silversides) constituted the primary available forage for Delta game fish and other wildlife.





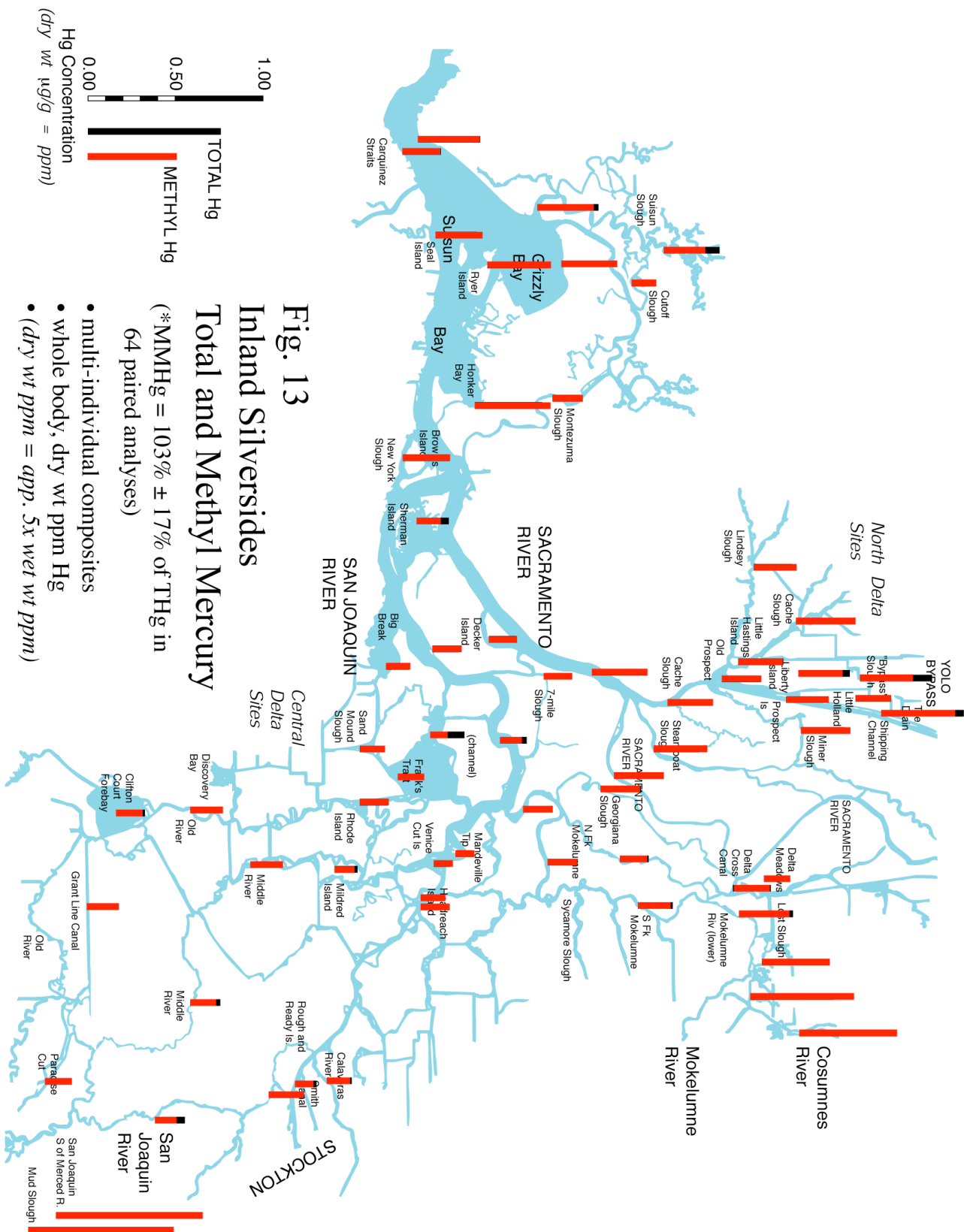




Fig. 14
Inland Silversides
Total Mercury
(THg QAOQC tighter than MeHg)

- multi-individual composites
- whole body, dry wt ppm Hg
- (*dry wt ppm = app. 5x wet wt ppm*)

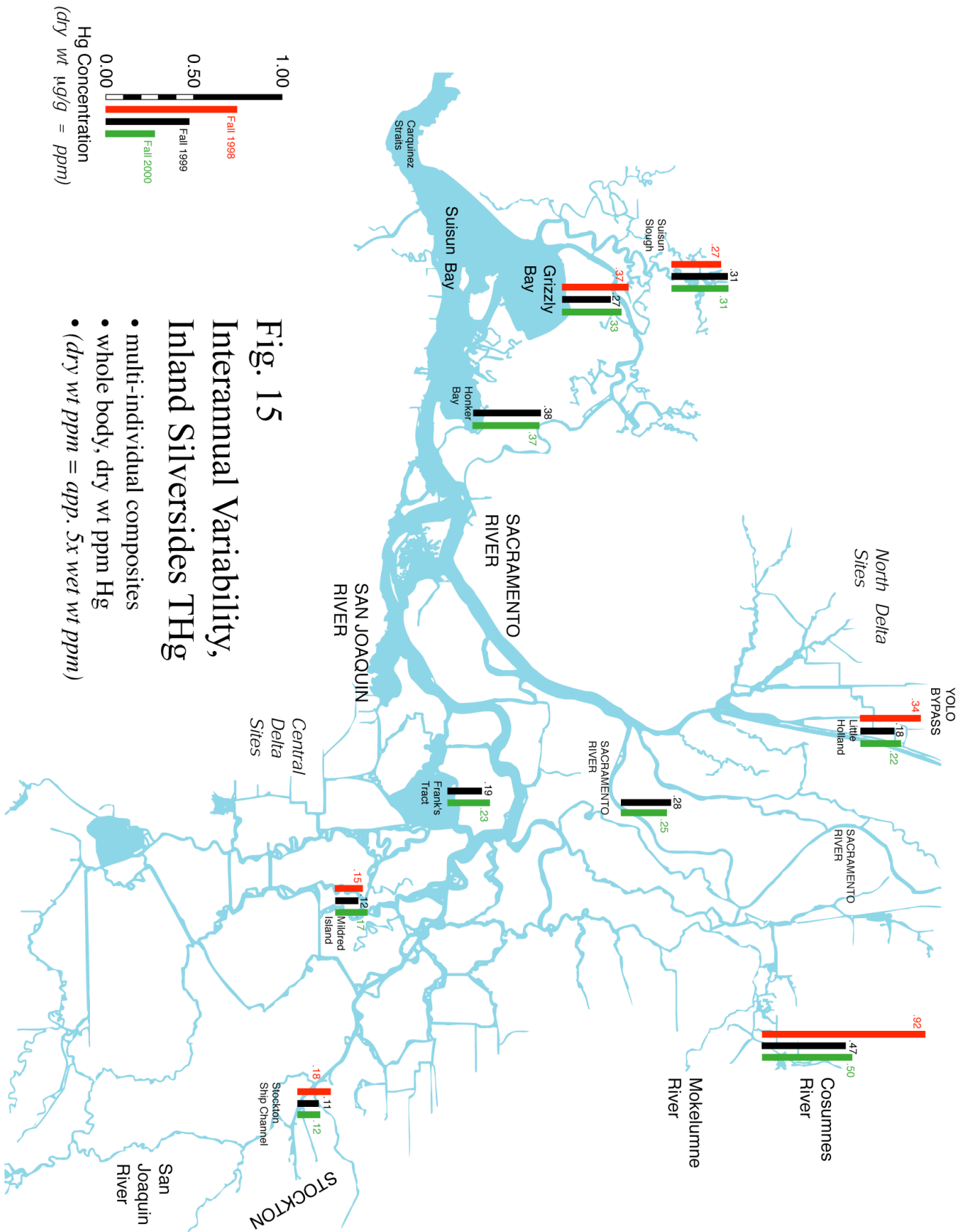
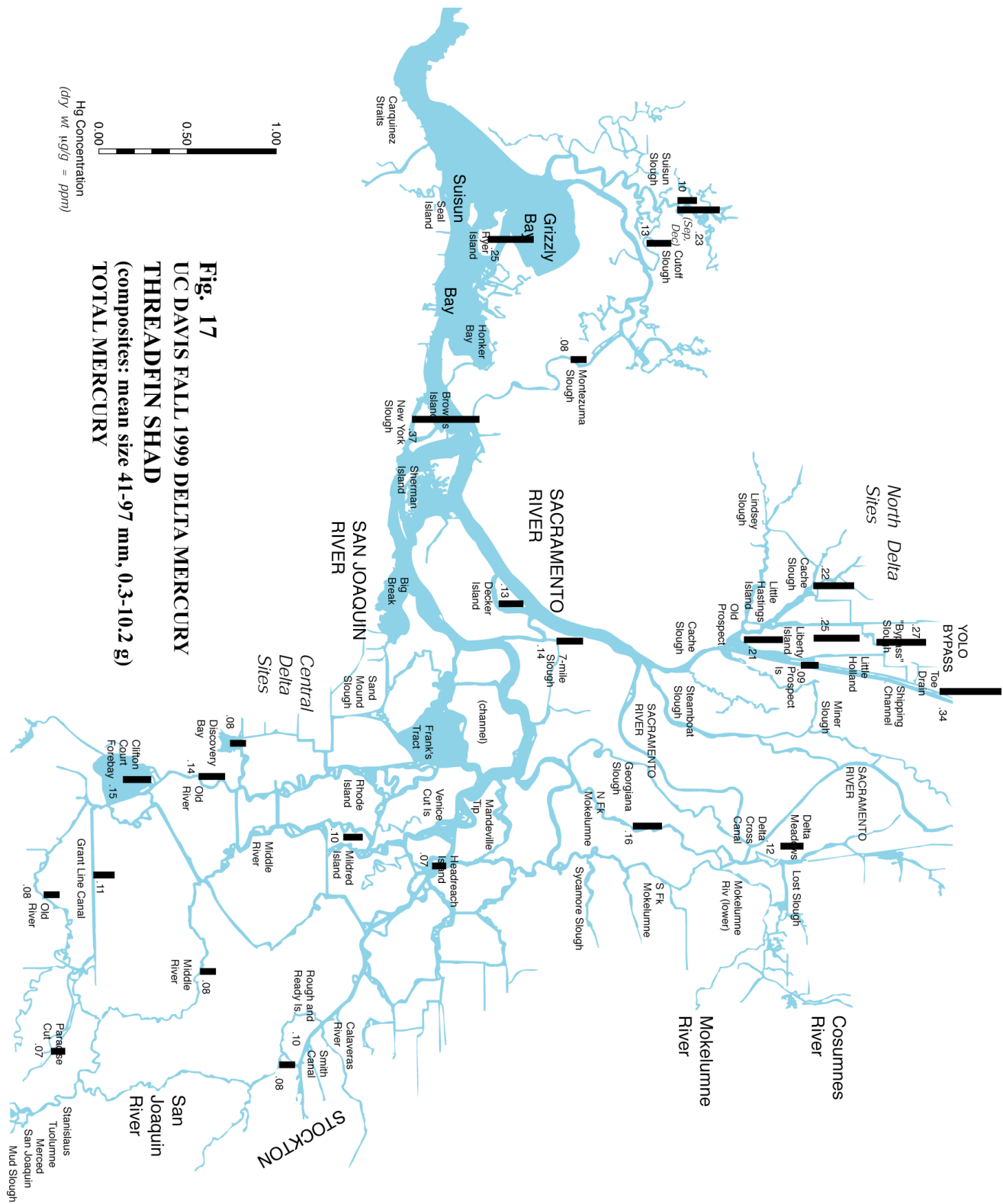


Fig. 15
Interannual Variability,
Inland Silversides THg

- multi-individual composites
- whole body, dry wt ppm Hg
- (dry wt ppm = app. 5x wet wt ppm)



Fig. 16
UC DAVIS FALL 1999 DELTA MERCURY
SIGNAL CRAYFISH (tail muscle)
(means of app. 10 individual analyses per site)
(size range: 37-60 mm carapace, 20-70 g)
TOTAL MERCURY



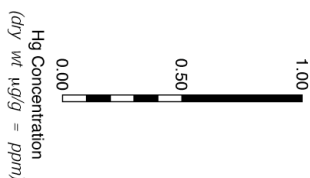


Fig. 18
UC DAVIS FALL 1999 DELTA MERCURY
JUVENILE LARGEMOUTH BASS
(composites: mean size 56-83 mm, 2.7-7.0 g)
TOTAL MERCURY



Fig. 19
UC DAVIS FALL 1999 DELTA MERCURY
BLUEGILL SUNFISH
(small composites: mean size 36-55 mm, 0.6-2.5 g)
(large composites: mean size 73-87 mm, 6.2-11.2 g)
TOTAL MERCURY

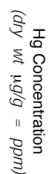


Fig. 20
UC DAVIS FALL 1999 DELTA MERCURY
GAMBUSIA (MOSQUITO FISH)
(composites: mean size 23-39 mm, 0.1-0.7 g)
TOTAL MERCURY

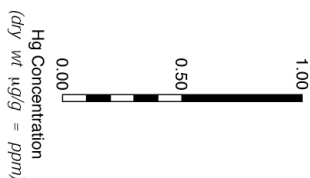
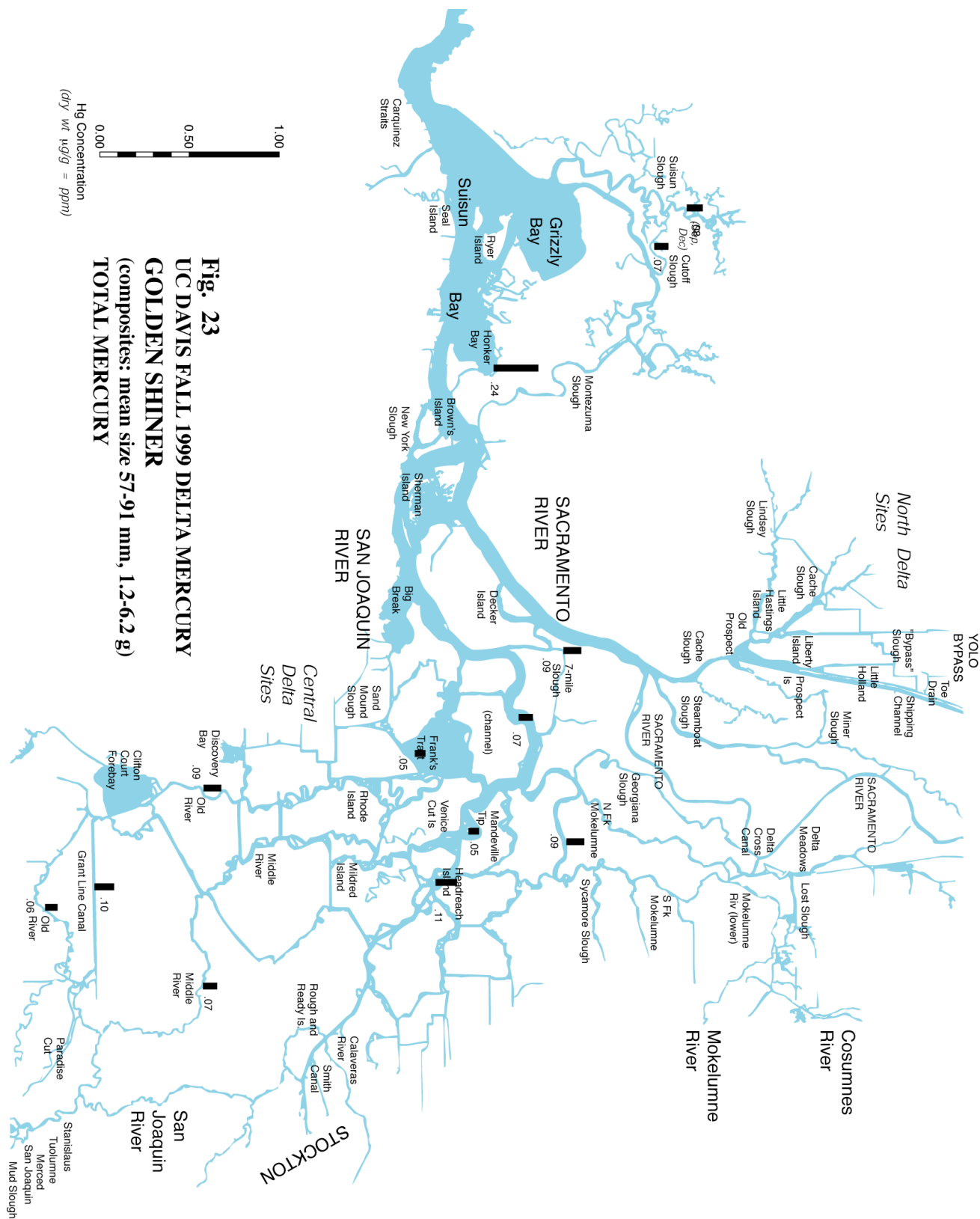
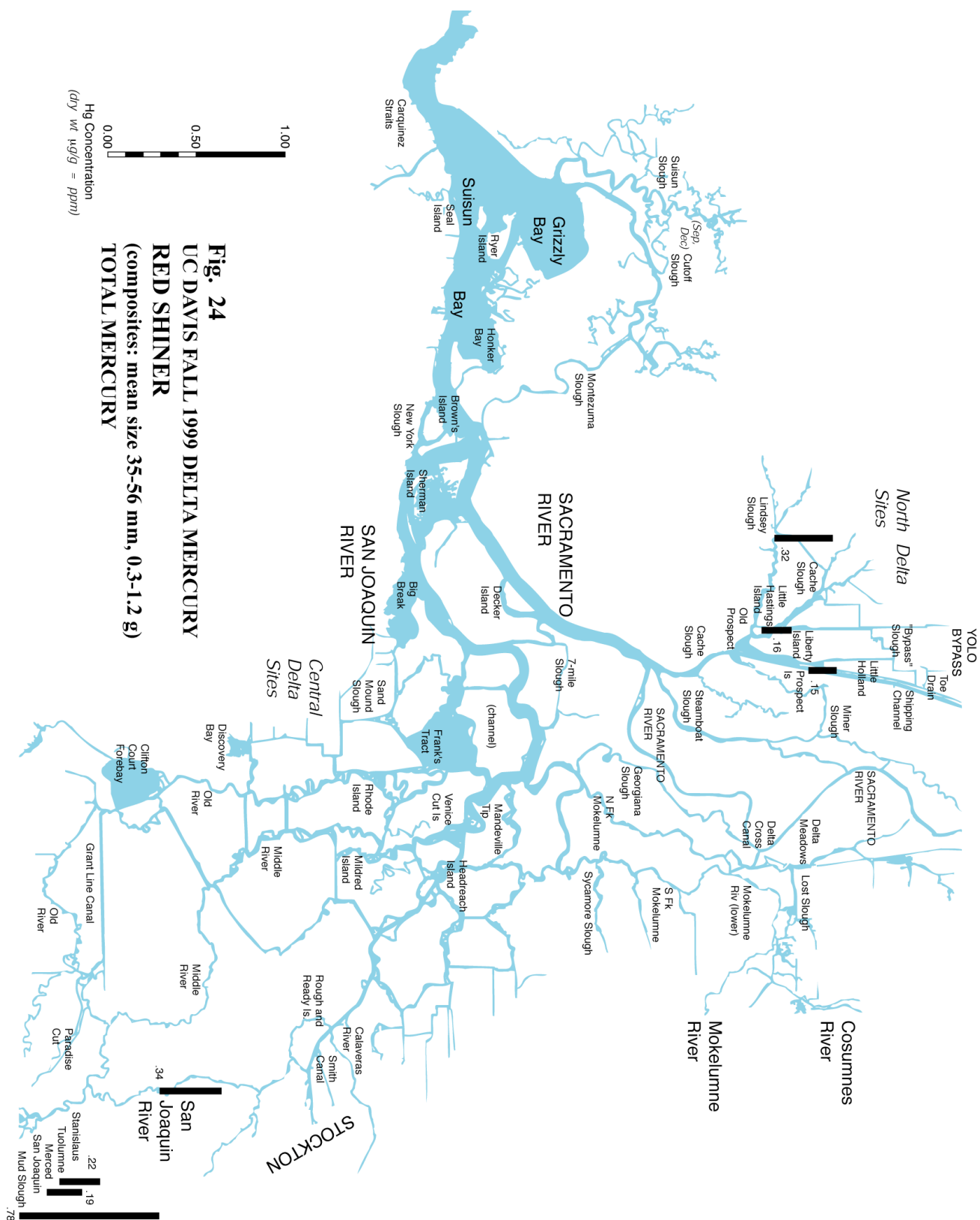


Fig. 21
UC DAVIS FALL 1999 DELTA MERCURY
YELLOWFIN GOBY
(small composites: mean size 52-88 mm, 1.0-5.6 g)
(large composites: mean size 90-130 mm, 5.6-16.8 g)
TOTAL MERCURY



Fig. 22
UC DAVIS FALL 1999 DELTA MERCURY
BIGSCALE LOGPERCH
(composites: mean size 58-72 mm, 1.2-2.6 g)
TOTAL MERCURY





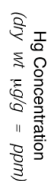


Fig. 25
UC DAVIS FALL 1999 DELTA MERCURY
CRANGON SHRIMP
(composites: mean size 42-63 mm, 0.1-1.6 g)
TOTAL MERCURY

Summary and Conclusions

The UC Davis study in the Sacramento-San Joaquin Delta generated findings that are generally consistent with and supportive of research by the multi-investigator CALFED directed action project. Results indicate that seasonal loading of Hg from tributary inflows may play an important role in the Hg cycling of the system. Flooded Delta tracts were indicated to function generally as net sources of MeHg. Tracts dominated by sand flats or mud flats were found to export MeHg in conjunction with large volumes of low to moderate concentration sediments, transported into the water column through wind and wave resuspension. In contrast, heavily vegetated, flooded wetland tracts appeared to function as traps for particulates and associated THg. These habitats were also indicated to promote relative Hg methylation and contribute to the export of elevated MeHg concentrations associated with reduced loads of particulates.

In apparent contrast with the flooded tract sediment and water findings, a wide range of lower trophic level biota were found to exhibit spatial Hg bioaccumulation trends indicating no apparent localized Hg enhancement in relation to wetland habitats. This was attributed to vigorous tidal mixing into larger Delta regions of MeHg that originated primarily in the flooded tracts. However, even regions of the Delta which included numerous well vegetated, flooded wetland tracts were not always found to demonstrate corresponding elevations in Hg bioaccumulation. Most perplexing was the finding of consistently lowest Hg bioaccumulation for the entire system throughout much of the South and Central Delta, where we had hypothesized that some of the most elevated Hg bioaccumulation might occur. The regions with most highly elevated biotic Hg identified in this work can instead be characterized as being dominated by ongoing new inflows of Hg from upstream San Francisco Bay-Delta tributaries. Inputs of both elemental Hg from historic gold mining in the Sierra Nevada and abandoned mercury mine cinnabar in the Coast Ranges appear to be of importance. This suggests that upstream remediation efforts on either side of the watershed may be more regionally meaningful than previously anticipated. A secondary zone of relatively elevated Hg bioaccumulation occurred in the estuarine entrapment / salinity transition zone.

The apparent contradiction between low Hg bioaccumulation in organisms and apparently high MeHg production and export in the Central Delta region highlights the potential complexities of Hg cycling. One possible explanation for the apparent “Central Delta depression” phenomenon is the highly organic nature of the peat-based soils in the vegetated tracts of this region. While these soils may be conducive to Hg methylation, they may also bind MeHg sufficiently to reduce its availability for bioaccumulation. Organic carbon in sediments and, particularly, the water column has been documented to strongly and negatively influence the bioavailability of MeHg to lower trophic level organisms (e.g. Monson and Brezonik 1999, Sjoblom *et al.* 2000, Snodgrass *et al.* 2000, Lawrence and Mason 2001). Thus, the highly organic flooded wetland tracts may be net producers of MeHg, but not in a form that is highly available for uptake by biota. Alternatively, or in conjunction with the potential organic carbon binding mechanism, if greater densities of algae and/or general biomass are found to be present in this Central region of the Delta, MeHg biodilution may be playing a role in the anomalously low bioaccumulation trend there (e.g. Lawrence and Mason 2001, Pickhardt *et al.* 2002).

Conceptual model based on this work

The various flooded wetland tracts of the Sacramento-San Joaquin Delta receive seasonal winter loadings of Hg proportional to their depositional characteristics and, particularly, their proximity to elevated-Hg tributary inflows. Additional loading or loss of THg and MeHg may occur in relation to ongoing Hg redistribution within the system, a function of localized erosional and depositional patterns. Some direct import of MeHg occurs from the tributary inflows. The Cosumnes River, Yolo Bypass, and Sacramento River appear to be the most important ongoing sources of new Hg to the system. Some of this Hg passes on to San Francisco Bay. Of the THg that deposits in flooded Delta tracts, a portion is methylated in the sediments, primarily linked to the bacterially mediated reduction of sulfur. Where methylation exceeds MeHg breakdown processes, a portion of the sediment net MeHg production may cross the sediment:water interface or be resuspended into the water column. A portion of this aqueous MeHg is locally bioaccumulated and recycled; a portion is exported from the tracts to the wider Bay-Delta by tidal currents. Flats-type flooded tract habitats may function as exporters of low to moderate concentration MeHg, associated with large loads of resuspended particulates. Heavily vegetated wetland tracts are traps for THg, sites of enhanced methylation, and exporters of elevated MeHg concentrations associated with reduced loads of particulates. Relative methylation, bioaccumulation, and export loading vary with season, tract habitat, localized limnological and food web characteristics, and tract location relative to primary upstream Hg loading flows. Low trophic level biota provide useful measures of relative biological MeHg exposure and accumulation, both spatially and temporally.

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